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Poisson's Ratio of Some Structural Alloys for Large Strains

By Ambrose H. Stang, Martin Greenspan, and Sanford B. Newman

Values of Poisson's ratio, as well as ordinary stress-strain properties, for tensile strains as high as 18 percent, were determined on sheets of aluminum alloys 24ST and 24SRT, chrome-molybdenum steel plate, and structural and fully killed low-carbon steel plate.

I. Introduction

1. General

n 1943 the Bureau decided to undertake an stigation on the elastic, and especially the stic, properties of various materials under ple tension, with particular reference to the iation of Poisson's ratio with axial strain for e strains. Shortly thereafter the Army Air ves Matériel Command expressed interest in project, and the work was carried on as a perative enterprise. The pressure of other vities made it necessary to restrict the inves- tion mainly to the materials in which the tériel Command was immediately interested; se were aluminum alloys 24ST and 24SRT et in several thicknesses and chrome-molyb- um steel plate 1/4 in. thick. Some additional lts, obtained on structural steel angles and es and on a fully killed low-carbon steel in nection with other investigations, are included his paper.

Very few values of Poisson's ratio in the plastic ge for structural materials have been published. sells and MacGregor [1] [1] report results for one cimen of nickel-chrome-molybdenum steel and nk [2] for one specimen of mild steel.

Figures in brackets indicate the literature references at the end of this r.

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2. Nomenclature

The term "stress" is here used to denote the stress based on original cross-sectional area. The term "strain" refers to the classical "extension," namely, the change in length of the gage line, reckoned from the original length, divided by the original length. The "axial strain," ϵ_a, is the strain parallel to the axis of the specimen and the load, and is here always positive as all the specimens were tested in tension. The term "lateral contraction" denotes the transverse strain, ϵ_l, which is always negative in these tests, along the width of the specimen in the case of sheet specimens, and the average value for all directions at right angles to the axis of the specimen in the case of round specimens.

The literature fails to disclose any accepted convention for the definition of Poisson's ratio for finite strains. The choice of a definition would, of course, be influenced by the definition adopted for strain itself. For the present purpose it was considered simplest to take Poisson's ratio, ν, as

$$\nu = -\epsilon_l/\epsilon_a.$$

The data are presented in such a manner that they may be readily expressed in terms of any alternate expressions for strain and Poisson ratio that one may adopt.

The term "direction", in obvious context denotes the angle between the direction of rolling of the material and the axis of the specimen (the load), in the plane of the sheet or plate. These rolled materials are assumed to be orthotropic, with two planes of symmetry perpendicular to the plate, one parallel to, and one perpendicular to the axis of rolling. Thus specimens whose axes make equal but opposite angles with the direction of rolling are equivalent, or have the same direction, and the possible directions lie between 0° and 90° only.

The standard deviation, σ, of a set of n quantities $X_i (i=1,2, \ldots n)$ is the root-mean-square deviation of the X_i from the average $\overline{X}$. This is [3],

$$\sigma = \left[\frac{\sum_{i=1}^{n}(X_i - \overline{X})}{n}\right]^{1/2}.$$

If the distribution of the x_i is normal, about two-thirds of the X_i lies between $\overline{X}-\sigma$ and $\overline{X}+\sigma$. In an actual case less than two-thirds of the X_i lies between these limits.

II. Materials and Specimens

The materials tested were aluminum alloy 24ST sheet in six thicknesses, aluminum alloy 24SRT sheet in two thicknesses, chrome-molybdenum steel plate 1/4 in. thick, fully killed low-carbon steel plates 1 1/2 in. thick, and structural-steel plates 3/8 in. thick and angles 1/2 in. thick. The number of specimens of each is given in table 1.

TABLE 1.—*Number of specimens tested*

[Direction refers to angle between direction of rolling and direction of tensile load]

Direction	0°	15°	30°	45°	60°	75°	90°
Nominal thickness	Number of specimens						
ALUMINUM ALLOY 24ST SHEETS							
in.							
0.022	2			2			2
.032 (1)[a]	2	2	2	2	2	2	2
.032 (2)	4			2			4
.064	4			2			4
.081	3			2			3
.092	2			2			2
.125	3			2			3
ALUMINUM ALLOY 24SRT SHEETS							
in.							
0.025	2			2			
.040	2						
CHROME-MOLYBDENUM STEEL PLATE							
0.25	2			2			
CARBON-STEEL, FULLY KILLED PLATES							
1.50	6[b]						
1.50	6			6			
STRUCTURAL LOW-CARBON STEEL PLATES AND ANGLES							
0.375	3						
.50	3						

[a] Specimens (1) and (2) were not from the same sheet.

[b] These 6 specimens were tested at a temperature of −44° C. All other specimens were tested at room temperature.

Most of the sheet material was tested in the three directions 0, 45, and 90 degrees, but one sheet of aluminum alloy 24ST, 0.032 in. thick, was tested in seven directions 15 degrees apart, as shown in table 1.

The chrome-molybdenum steel was SAE X4130, condition *A* (annealed) and was supposed to comply with Army-Navy specification AN QQ–S–685.

The carbon steel, fully killed, was from a lot specially rolled for another investigation and had the following composition: Carbon 0.22 percent, manganese 0.56 percent, phosphorus 0.016 percent, sulfur 0.028 percent.

The low carbon structural steel, complied with ASTM Specification A7–42 for Steel for Bridges and Buildings. The chemical composition was carbon 0.25 percent, manganese 0.39 percent, phosphorus 0.011, and sulfur 0.036 percent.

The specimens from the fully killed carbon steel plates, 1.5 in. thick, were of circular cross section and 12 in. long over-all. The diameter of the 9 in. long reduced portion was 1⅛ in., and the ends were 1⅜ in. in diameter.

The other specimens were all of the as-rolled thickness of the material. They were 16 in. long over-all, 2 in. wide at the ends, and had a width of 1.75 in. in the 5 in. long reduced portion.

III. Methods of Test

1. Loading

Except as noted below, all of the sheet and plate specimens were loaded in either of two Baldwin-Southwark hydraulic testing machines (capacities 20 kips and 60 kips) equipped with Tate-Emery weighing systems. In the case of the 0.032-in. sheet of 24ST from which specimens were taken in seven directions, the loading in the elastic range was accomplished by means of a single dead weight of 953.0 lb., corresponding to a stress of about 17 kips/in^2.

The sheet and plate specimens were in all cases held in 2-in.-wide Templin grips, capacity 20 kips. The round steel specimens were held in threaded adapters and loaded in an Amsler horizontal hydraulic testing machine, capacity 100 kips.

Except in the case of six of the fully killed carbon steel specimens, all tests were performed at room temperature. The steel specimens were tested in connection with another investigation and the tests were performed at a temperature of about −44° C. Preliminary tests had indicated that this fully killed steel was as ductile at −44° C as many ordinary ship steels are at room temperature, and the tensile tests confirmed this conclusion. The low temperature was maintained by solid CO_2 in an insulated box surrounding the specimen, and was measured by means of two copper-constantan thermocouples attached one near each end of the reduced portion of the specimen.

Most of the specimens were strained, in the elastic range, at a rate of about 0.8 percent per minute. Of the aluminum alloy 24ST, four specimens, two at 0 and two at 90 degrees, from each of two sheets (0.032 in. and 0.064 in.) were strained at a rate of about 3.2 percent per minute. This 4 to 1 variation in speed had no appreciable effect on the values of Poisson's ratio obtained, and therefore, speed over the range of low speeds used in these tests was not considered a significant variable.

2. Strain Measurements

(a) Elastic Strains

Method a–1.—In most cases these were determined by means of Tuckerman optical strain gages, 1-in. gage length. There were two gages parallel to the axis of the specimen, opposite each other at midwidth; these had 0.5-in. lozenges. Two gages having 0.2-in. lozenges were similarly disposed at right angles to the axis of the specimen. The load was applied slowly and then held constant while the strain gages were read.

Method a–2.—In the case of the 0.081-in. 24ST sheet and the fully killed carbon steel, the elastic strains were determined by means of SR–4 electric strain gages of various types (*A*–1, *A*–3, *A*–5) used in conjunction with SR–4 portable strain indicators. The disposition of the gages was the same as of the Tuckerman gages of method. a–1.

(b) Small Plastic Strains

Method b–1.—Wherever method a–1 had been used for the elastic strains, the same Tuckerman gages were used in the intermediate range. Each

gage was reset to a point near the beginning of the range and initial readings were taken on all four gages. The testing machine was then operated at a constant rate of head separation, and simultaneous readings of load and of transverse strain on one side of the specimen were taken at predetermined readings of the axial gage on the other side of the specimen. When the range of the gages was nearly exhausted, the straining was stopped and the load reduced slightly and held constant as the four gages were read again. The bending in the specimen was determined from the readings of the mutually opposite gages. The readings that had been taken on only one side of the specimen were corrected to the average value. This correction was usually small, rarely exceeding 1 percent. The axial strain amounted to about 3 percent as the straining was stopped for this series of measurements.

Method b–2.—The electric strain gages of method a–2 were employed until the gages failed, usually at an axial strain of about 1 percent for tests at −44° C and of about 2.5 percent for tests at room temperature.

(c) Large plastic strains

Method c–1.—Preliminary tests showed that the larger plastic strains were not uniform along the length or width of the specimen, so that values of Poisson's ratio computed from the strains at midwidth of the specimen were irregular. However, satisfactory results could be obtained by using average strains over a "gage square" about as wide as the specimen. Such a square was scribed on one side of the specimen at midlength. It consisted of three axial and three transverse gage lines, spaced 3/4 in. apart. The ends of the axial gage lines were marked by the two outside transverse gage lines, and the lengths of the axial lines were measured before and after straining by means of a traveling microscope having a least count (estimated place) of 0.001 mm. The width of the specimen at each of the three transverse gage lines was measured before and after straining by means of a special outside micrometer constructed from two dial gages having a least count (estimated place) of 0.00001 in. After each increment of strain the specimen was removed from the testing machine and the gage lines were measured. The average axial and transverse permanent sets corresponding to the load attained when straining was stopped were computed from these data, the set of the middle gage line in either direction be given double weight in obtaining the aver The total strain in either direction was take the average permanent set plus the recov strain for that direction. The recovery str were computed from the slopes of the l recovery strain lines obtained by means of Tuck man strain gages during unloading of the speci just prior to removing it from the testing mach for measurement of set.

This procedure is based on the comm observed facts (see e. g. [4]) that for ductile me an interrupted tensile test gives a family of str strain curves of which the envelope is the str strain curve for a continuous test, and that stress-recovery strain curve is practically lin Small effects, such as elastic hysteresis and elastic after-effect, are neglected.

This method gave very satisfactory results e though the axial strains were measured on one of the specimen only. The indications were t the bending of these thin specimens at high str were inconsiderable. However, the method time-consuming and tedious. Furthermore, intermittent loading of the aluminum alloys p duced a pronounced tendency toward the for tion of Lüders' lines [5]. A specimen which h been stretched 2 or 3 percent and then unlo usually exhibited very distinct Lüders' lines reloading. These appeared one or only a few time, accompanied by small but abrupt variati in the load and frequently by clicks. A typical of Lüders' lines is shown in the photograph, fig 1. The angle between the trace of the slip pl on the surface and the axis of the specimen was same, about 60 degrees, for all specimens, direction and the thickness of the speci seemingly having no effect. These Lüders' li produced no irregularity in the values of Poiss ratio provided the gage square was either co pletely full or completely devoid of the lines. T data obtained when the gage square was partia covered with lines had to be discarded. Occasi ally, after the Lüders' lines had completely cove the surfaces of the specimen, they disappea upon further straining, and in some cases a sec set would eventually appear.

Method C–2.—After the transfer strain ga described in [6] had been developed they were u for the remainder of the tests. The axial stra were measured by means of three gages on one s of the specimen and the transverse strains by me

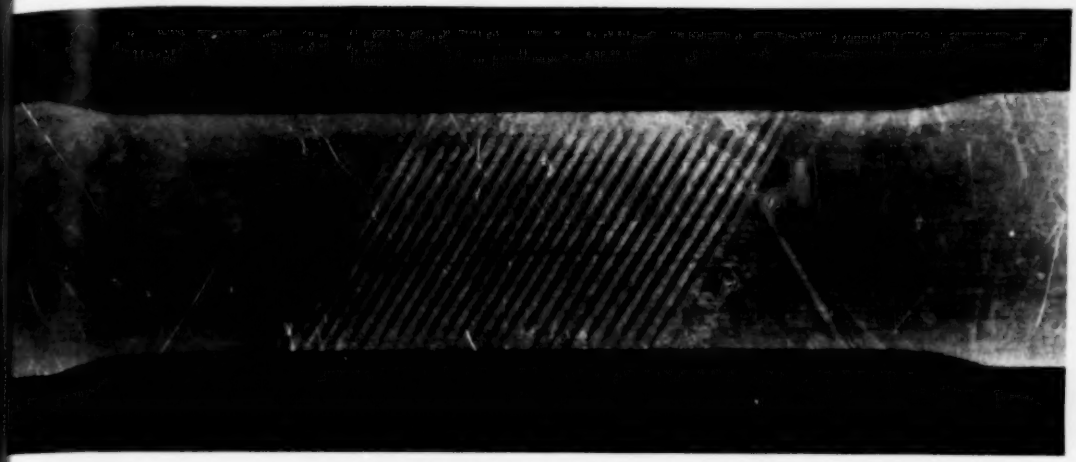

FIGURE 1.—*Lüders' lines on aluminum alloy 24ST.*

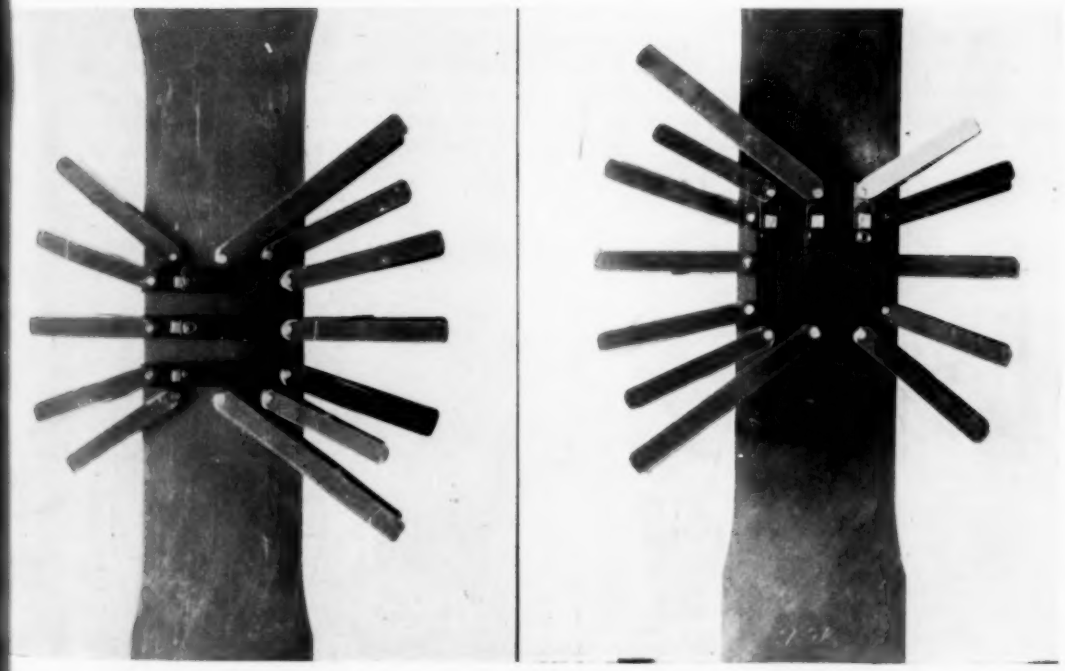

FIGURE 2.—*Transfer strain gages on a tensile-test specimen of aluminum alloy 24ST sheet.*

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three gages on the other side of the specimen as shown in figure 2. This method allowed a continuous test and gave good results, but was time-consuming and tedious.

3. Computations

Young's modulus of elasticity, E_A and the transverse modulus of elasticity, "E_T (slope of the linear part of the axial stress-transverse strain curve) were obtained from residual plots [7]. Poisson's ratio in the elastic range was taken as $\nu_0 = -E_A/E_T$.

The axial stress was plotted against axial strain on semilogarithmic paper (strain on log scale) and faired. The lateral contraction was plotted against axial strain on logarithmic paper and Poisson's ratio was computed at various points along the faired curve.

IV. Results and Discussion

1. Variation of Properties With Direction in a Sheet of Aluminum Alloy 24ST

The elastic constants, in terms of Young's modulus, E_A, transverse modulus, E_T, and Poisson's ratio are shown in figure 3. The circles represent the results of the measurements. The curves are of the type that would be expected for a homogeneous orthotropic material [8] having two planes of symmetry perpendicular to the sheet, one parallel to, and one perpendicular to the direction of rolling. The curves for Young's modulus and the transverse modulus were fitted to the data by least squares; the curve for Poisson's ratio was computed from the other two. It is evident from figure 3 that the sheet has a definite elastic anisotropy, although it is so small, especially in consideration of the scatter between two specimens in the same direction, that it would scarcely be noticed if the loads were applied in a testing machine rather than by dead weights.

The results in the plastic range are shown in figure 4, in which each curve is an average for two specimens. The scatter to be expected in a group of nominally identical specimens of 24ST is discussed in following sections. It is seen that for a given direction Poisson's ratio increases, reaches a maximum, and then decreases as the axial strain increases. This behavior is characteristic of practically all of the specimens tested and is qualitatively the same as for an ideal case of no plastic dilatation in an isotropic material, as will be shown in section V. The axial-stress axial-strain curves are shown in figure 4 for directions 0, 15, 45, and 90 degrees. The 60- and

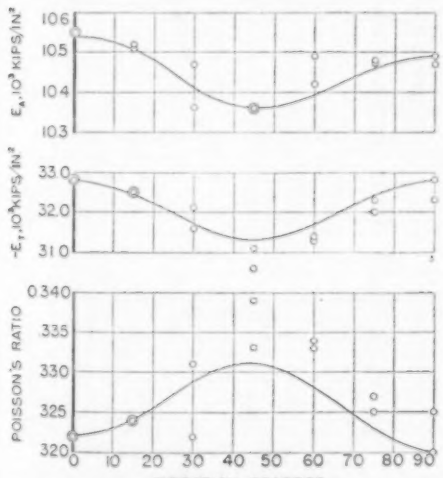


FIGURE 3.—*Variation of elastic constants with direction in aluminum alloy 24ST sheet, 0.032 in. thick.*

The circles represent the measured values.

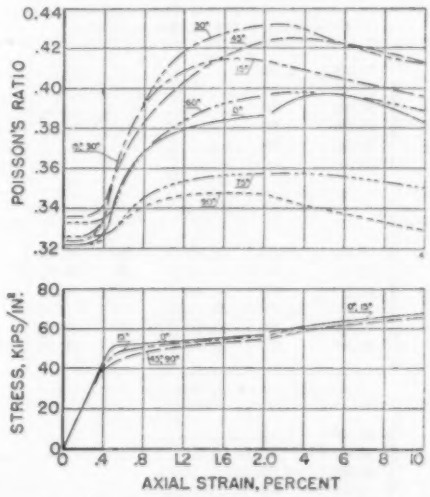


FIGURE 4.—*Aluminum alloy 24ST sheet, 0.032 in. thick.*

Each curve represents the average for two specimens. Note change of axial-strain scale at 2 percent.

75-degree curves are identical and lie just above the 45- and 90-degree curve. The 30-degree curve lies between the 15-degree curve and the 60- and 75-degree curve, closer to the latter. These curves show that the tensile stress-strain curves vary with direction most rapidly near the knees of the curves for directions within about 30 degrees from the direction of rolling.

TABLE 2.—*Young's modulus of elasticity and Poisson's ratio for specimen tested in the elastic range*

Nominal thickness	Young's modulus	Direction, degrees: 0		45		90	
		Poisson's ratio	Young's modulus	Poisson's ratio	Young's modulus	Poisson's ratio
ALUMINUM ALLOY 24ST							
In.	*Kips/in.²*		*Kips/in.²*		*Kips/in.²*	
0.022	10,600	0.321	10,700	0.329	10,500	0.310
	10,600	.323	10,500	.331	10,700	.323
.032	10,400	.329	10,400	.318	10,300	.322
	10,300	.319	10,500	.326	10,400	.330
.064	10,500	.323	10,400	.331	10,400	.327
	10,700	.328	10,500	.328	10,500	.320
.081	10,000	.315	10,000	.320	9,900	.314
	10,100	.312	9,900	.312	10,000	.316
	10,000	.311	----------	----------	9,900	.314
ALUMINUM ALLOY 24SRT						
0.025	10,500	0.321	10,400	0.330	10,400	0.325
	10,500	.316	10,300	.317	10,400	.320
.046	10,500	.333	----------	----------	10,400	.326
	10,500	.332	----------	----------	10,400	.328
CHROME-MOLYBDENUM STEEL						
0.25	30,700	0.268	30,400	0.289	31,000	0.274
	30,500	.276	30,300	.289	31,100	.282
CARBON STEEL, FULLY KILLED, AT −44° C						
1.50	29,600	0.269	----------	----------	----------	----------
	29,500	.280	----------	----------	----------	----------
	29,200	.274	----------	----------	----------	----------
	29,000	.267	----------	----------	----------	----------
	29,800	.281	----------	----------	----------	----------
	29,100	.265	----------	----------	----------	----------
CARBON STEEL, FULLY KILLED, AT ROOM TEMPERATURE						
1.50	28,850	0.270	28,570	0.263	28,220	0.270
	28,820	.267	28,450	.267	28,430	.268
	28,480	.273	28,500	.263	28,500	.274
	28,350	.267	28,620	.270	28,500	.275
	28,500	.269	28,410	.274	28,430	.279
	28,480	.277	28,400	.274	28,480	.271
STRUCTURAL STEEL PLATES AND ANGLES						
0.375	30,100	0.256	----------	----------	----------	----------
	29,800	.265	----------	----------	----------	----------
	30,300	.270	----------	----------	----------	----------
.50	29,500	.265	----------	----------	----------	----------
	29,300	.260	----------	----------	----------	----------
	29,800	.271	----------	----------	----------	----------

2. Aluminum Alloy 24ST

The values of Young's modulus of elasticity and Poisson's ratio in the elastic range for the individual specimens are given in table 2.

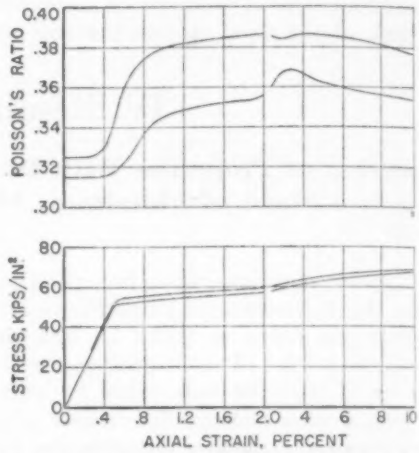


FIGURE 5.—*Aluminum alloy 24ST sheet, direction 0 degrees.*

The upper curve is the average plus the standard deviation, and the lower curve is the average minus the standard deviation for 9 to 12 specimens 0.022, 0.032, 0.064, or 0.081 in. thick. Note change of axial-strain scale at 2 percent.

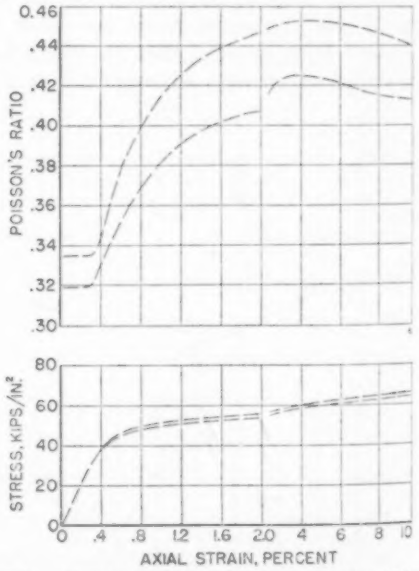


FIGURE 6.—*Aluminum alloy 24ST sheet, direction 45 degrees.*

The upper curve is the average plus the standard deviation, and the lower curve is the average minus the standard deviation for 8 to 10 specimens 0.022, 0.032, 0.064, or 0.081 in. thick. Note change in axial-strain scale at 2 percent.

The 0.092- and 0.125-in.-thick specimens were not tested in the elastic range.

The averages, plus or minus standard deviations, of the stress and Poisson's ratio are shown in figures 5, 6, and 7 for directions 0, 45, and 90 degrees, respectively. The scatter in the values of stress and Poisson's ratio for a given axial strain was no greater in the group consisting of specimens 0.022, 0.032, 0.064, and 0.081 in. thick than it was for specimens of the same thickness; the results for these four thicknesses were therefore averaged.

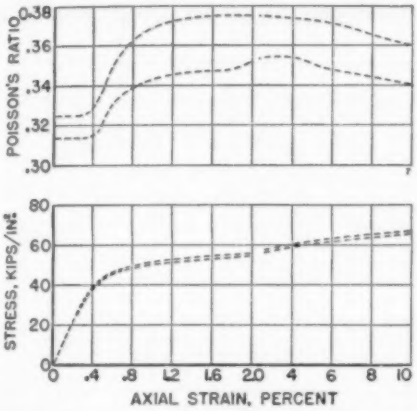


FIGURE 7.—*Aluminum alloy 24ST sheet, direction 90 degrees.*

The upper curve is the average plus the standard deviation, and the lower curve is the average minus the standard deviation for 9 to 12 specimens 0.022, 0.032, 0.064, or 0.081 in thick. Note change of axial-strain scale at 2 percent.

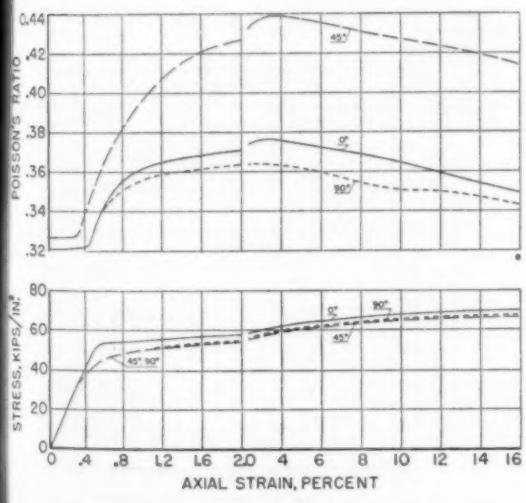


FIGURE 8.—*Aluminum alloy 24ST sheet.*

Average values for the specimens of figures 5, 6, and 7. Note change of axial-strain scale at 2 percent.

Somewhat less than two-thirds of the data lies in the dispersion band bounded by the two curves in each case. The results are summarized in figure 8, which shows the average values of the stress and of Poisson's ratio for each of the three directions.

The results for the individual specimens 0.092 and 0.125 in. thick are shown in figures 9 and 10, respectively.

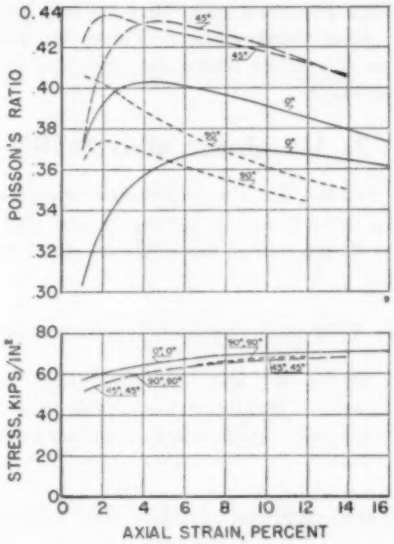


FIGURE 9.—*Aluminum alloy 24ST sheet, 0.092 in. thick.*

Two specimens each at 0, 45, and 90 degrees.

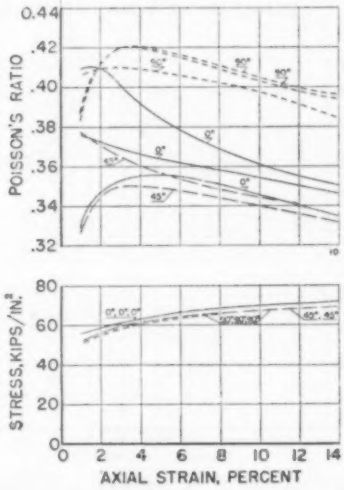


FIGURE 10.—*Aluminum alloy 24ST sheet, 0.125 in. thick.*

Three specimens each at 0 and 90 degrees, 2 at 45 degrees.

In many cases there are large discrepancies in the values of Poisson's ratio for two nominally identical specimens, especially for the smaller plastic strains. The accumulation of error that occurs when one strain is divided by another in the process of computing Poisson's ratio accounts for a considerable part of this discrepancy. It is felt, however, that the results indicate an inherent variability in the material itself which is greater as regards Poisson's ratio than as regards stress, for a given axial strain. These remarks also apply to the other materials discussed in subsequent sections.

3. Aluminum alloy 24SRT

The results for the individual specimens are given in table 2 and in figures 11 and 12. Specimens at 45 degrees in the 0.045-in. sheet were not obtained.

4. Chrome-molybdenum steel

The results for the individual specimens are given in table 2 and figure 13. Tests in the plastic range of axial strain below 2 percent were not made.

5. Low-carbon steel, fully killed, at −44°C

All six of these specimens were parallel to the directions of rolling. They were tested at about −44° C. The values of Young's modulus and of Poisson's ratio in the elastic range are given in table 2. The results in the plastic range are shown in figure 14 as averages, plus or minus standard deviations.

These specimens were assumed to be transversely isotropic so that the dilatation could be computed as a function of axial strain. This was done by using the average values of Poisson's ratio for the six specimens. The results are shown by the upper curve (full line) of figure 15. The lower curve (full line) shows the elastic (recoverable) dilatation computed on the assumption that the modulus during the release of load, for axial strain

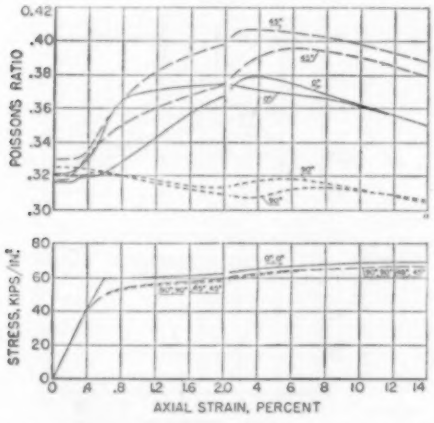


FIGURE 11.—*Aluminum alloy 24SRT sheet, 0.025 in. thick.*
Two specimens each at 0, 45, and 90 degrees. Note change of axial-strain scale at 2 percent.

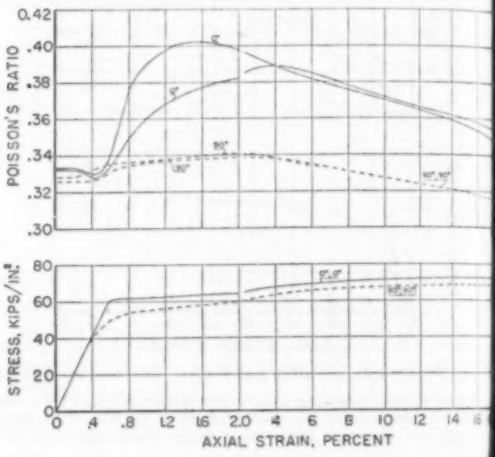


FIGURE 12.—*Aluminum alloy 24SRT sheet, 0.048 in. thi*
Two specimens each at 0 and 90 degrees. Note change of axial-strain sc
at 2 percent.

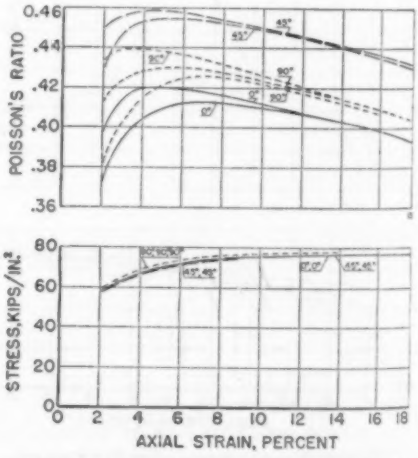
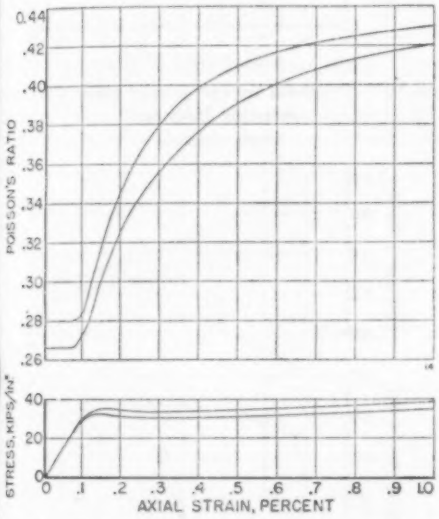


FIGURE 13.—*Chrome-molybdenum steel plate, 1/4 in. thick*
Two specimens each at 0 and 45 degrees, three at 90 degrees.

s than 1 percent was equal to the value of oung's modulus for the material. It is seen that er yielding has begun the permanent dilatation a large part of the total.

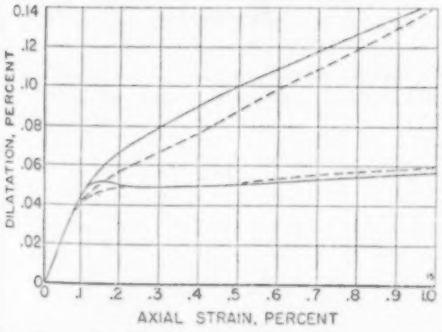
6. Low-carbon steel, fully killed, at room temperature

The results for the individual specimens are en in table 2. The averages, plus or minus ndard deviations, of the stress and Poisson's io are shown in figures 16, 17, and 18 for direcns 0, 45, and 90 degrees, respectively.



URE 14.—*Fully killed low-carbon steel plate, 1½ in. thick, at −44°C.*

e upper curve is the average plus the standard deviation, and the lower ve is the average minus the standard deviation for 6 specimens at 0 degrees.



URE 15.—*Fully killed low-carbon steel at −44° C (full line) and at room temperature (broken line).*

ilatation as a function of axial strain. The upper curve shows the total, the lower curve the elastic dilatation.

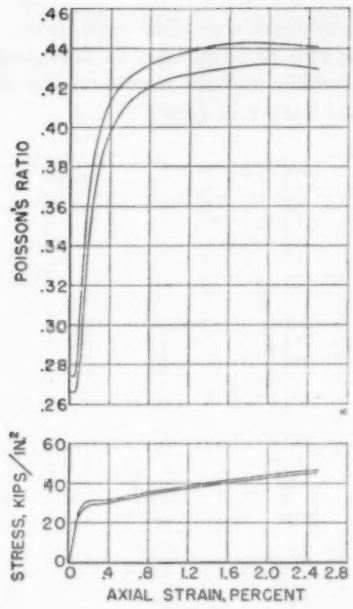


FIGURE 16.—*Fully killed low-carbon steel plates, 1.5 in. thick, direction 0 degrees*

The upper curve is the average plus the standard deviation, and the lower curve is the average minus the standard deviation for 6 specimens.

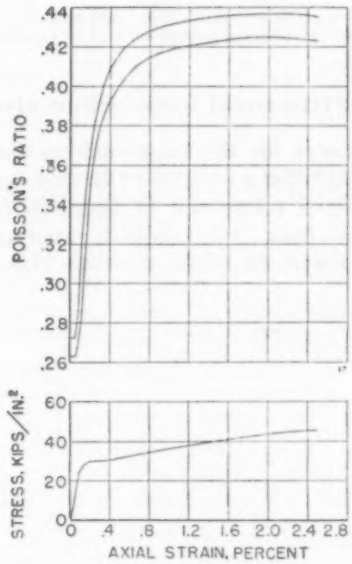


FIGURE 17.—*Fully killed low-carbon steel plates, 1.5 in. thick, direction 45 degrees*

The upper curve is the average plus the standard deviation, and the lower curve is the average minus the standard deviation for 6 specimens.

The dilatation was computed from average values for the 18 specimens as described in the previous section, and the results are shown by the broken-line curves in figure 15.

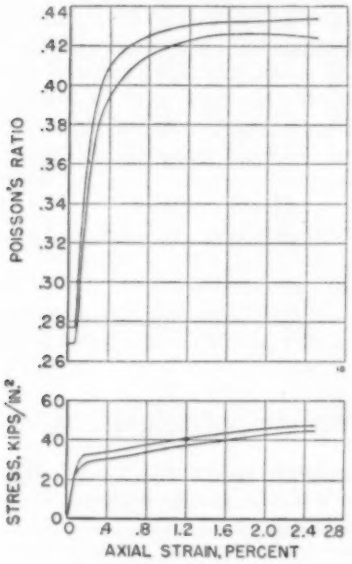


FIGURE 18.—*Fully killed low-carbon steel plates, 1.5 in. thick, direction 90 degrees*

The upper curve is the average plus the standard deviation, and the lower curve is the average minus the standard deviation for 6 specimens.

7. Structural low-carbon steel

The results for the individual specimens are given in table 2 and in figure 19 for three specimens from 3/8-inch plates and in figure 20 for three specimens from 1/2-inch-thick angles. These specimens were all at the direction of 0 degrees. Tests in the plastic range of axial strain beyond 2 percent were not made.

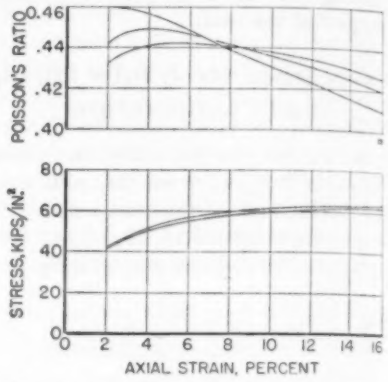


FIGURE 19.—*Structural low-carbon steel plates, 3/8-in. thick, direction 0 degrees.*

Three specimens

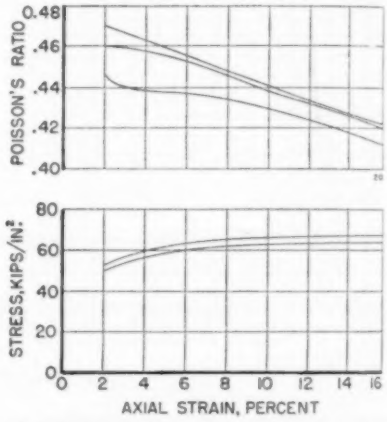


FIGURE 20.—*Structural low-carbon steel angles, 1/2-in. thick, direction 0 degrees.*

Three specimens

V. Appendix—Variation of Poisson's Ratio With Axial Strain in an Ideal Case

It is instructive to consider the variation of Poisson's ratio, ν, in a simple case, say a material having a stress-strain curve as shown in figure 21, which is a horizontal line in the plastic range and has a sharp knee. If the proportional limit corresponds to an axial strain of 0.005 and Poisson's ratio in the elastic range is 0.3, the elastic dilatation is 0.002 for axial strain, ϵ_a, greater than 0.005. The dilatation, δ, is

$$\delta=(1+\epsilon_a)(1-\nu\epsilon_a)^2-1,$$

from which

$$\nu=\frac{1-\left(\frac{1+\delta}{1+\epsilon_a}\right)^{1/2}}{\epsilon_a}.$$

If there is no plastic dilatation, $\delta=0.002$ for $\epsilon_a>0.005$, and the variation of ν with ϵ_a is as shown in figure 21. It is seen that ν rises from the elastic value of 0.3 to a maximum of 0.463 at about $\epsilon_a=0.05$, and then decreases readily.

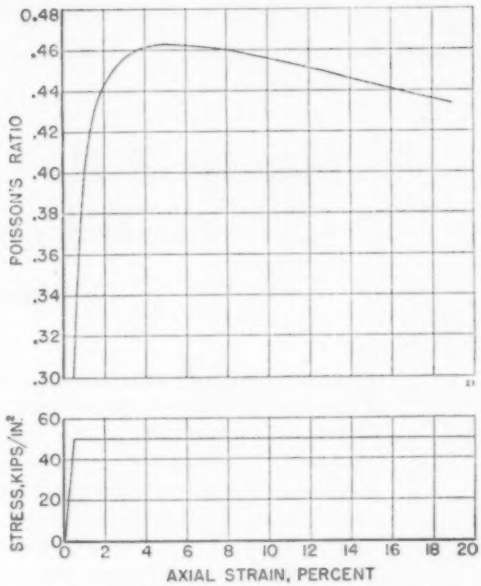


FIGURE 21.—*Variation of Poisson's ratio with axial strain in an ideal case.*

Elastic dilatation 0.2 percent for strains greater than 0.5 percent, no plastic dilatation

VI. References

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Electrode Function (pH Response) of Potash-Silica Glasses

By Donald Hubbard

The electrode function (pH response) of a series of potash-silica (K_2O-SiO_2) glasses was determined and a comparison made with the hygroscopicity of the glasses. All the K_2O-SiO_2 glasses investigated showed a very high hygroscopicity, with an accompanying sensitive pH response. However, between pH 2 and 4, glasses of 71.8 and 73.6 percent SiO_2 gave pH-response values higher than the 59 millivolts per pH predictable from the Nernst equation.

Electrodes prepared from all members of the series demonstrated large voltage departures from the straight-line relation with increasing alkalinity of the buffer solutions. For a glass of 75.76 percent SiO_2 content, the voltage departures were compared with the chemical durability of the glass and also with the sodium-ion concentration, $[Na^+]$, of the Britton-Robinson universal buffer solutions used. The voltage departures correlated with the magnitude of the attack much more convincingly than with the pNa.

For several chosen pH values, the voltage departures for the electrodes of these glasses when plotted with reference to their SiO_2 content gave curves that indicated a sharp change in slope near 74 percent of silica. A corresponding change in slope was also shown by the hygroscopicity-percentage-silica curve.

I. Introduction

The suitability of a glass for use in measuring the hydrogen-ion activity of aqueous solutions in accord with the dictates of the simplified Nernst equation, $\Delta E = 0.000198 T\text{pH}$, appears to be determined largely by two properties of the glass, namely, its water sorption (hygroscopicity) and the uniformity of its chemical durability when immersed in solutions varying in pH over an extended range. The absence of adequate hygroscopicity of the glass results in electrodes of high resistance whose pH responses fall appreciably below the theoretical value [1, 2, 3],[1] whereas conditions that cause changes in the chemical

[1] Figures in brackets indicate the literature references at the end of this paper.

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durability of the glass are accompanied by voltage departures [4, 5] that are roughly proportional to the magnitude of the change in durability [6]. In addition to the above electrical characteristics, some glasses under special conditions are believed to show specific equilibrative responses to ions other than hydrogen [7; 1, p. 267].

In the present investigation, a limited series of potash-silica (K_2O-SiO_2) glasses was studied with respect to each of the above properties.

II. Experimental Procedures

The hygroscopicity values were obtained by exposing powdered samples of the glasses to the high humidity furnished by a saturated solution of $CaSO_4.2H_2O$ thermostated in an air bath at 25° C. The glass samples were prepared by repeated crushing, in a steel mortar, and sieving through a Tyler standard 150-mesh sieve. Each sample consisted of approximately 1.5 grams of glass that had passed the sieve.[2] The samples were exposed in shallow weighing bottles for 1 and 2-hour periods. The resulting hygroscopicity values for the glasses are reported in terms of known factors, namely, weight of water sorbed times the density of the glass divided by the weight of the sample.

The humidity chamber consisted of a modified glass desiccator whose base was filled with the $CaSO_4.2H_2O$ solution. To hasten equilibrium and maintain uniformity, a small fan was mounted through a lucite bearing in the top of the vessel, and the inner walls were lined with a wick made from blotting paper.

The electromotive-force measurements were made with a Beckman pH meter, Laboratory Model G. Although the sensitivity of this instrument decreases for electrodes with resistances greater than 500 megohms, this was not a contributing factor to the results obtained on the K_2O-SiO_2 series because all the electrodes from these glasses exhibited low resistance. The glass electrodes were blown as thin-walled bulbs on the end of tubing made from the experimental glasses,[3] and the inner electrical connection was obtained by filling the bulb with mercury [8].

The chemical durability measurements were made by the interferometer method [5, 6, 9]. In order to have the results directly comparable with the work reported in the previous publications, the Britton-Robinson buffer mixtures [10] were used, and the temperature was maintained at 80°C±0.2°. Durability measurements for a particular composition, and for the pH range covered, were made on a single specimen of glass, which was reground and repolished after each test.

The glasses were prepared by C. A. Faick and analyzed by F. W. Glaze [11]. Glasses of SiO_2 content lower than 71.83 percent were very unstable as electrodes, and those containing over 83.07 percent were not made because of the high melting point, high viscosity, and consequent difficulty of fining.

[2] The results of a series of experiments, not reported here, indicate that reproducibility by this method of sample preparation is equal to that obtained by crushing and using a fraction passing one sieve and retained by another.

[3] Tubes of the experimental glasses were drawn by Thomas R. Talt, of the Bureau's glassblowing shop.

III. Results and Discussion

1. Hygroscopicity and pH Response

The data listed in table 1 and plotted in figure 1 give the hygroscopicity and accompanying pH response for the series of K_2O-SiO_2 glasses. To these have been added for comparison, similar data on Corning 015, an optical glass BSC 517, Pyrex, Vycor, and fused silica.[4] The last four glasses were included to complete a hygroscopicity–pH-response series [3]. For the K_2O-SiO_2 glasses the hygroscopicity was very high, and the electrodes prepared from them had a correspondingly sensitive pH response. However, the glasses of 71.8 and 73.6 percent SiO_2, although very sensitive, showed drifting voltages which gave rise to spurious pH responses, greater than those predictable from the Nernst equation. The electrodes from other members of the K_2O-SiO_2 series gave steady readings that very closely approxi-

[4] For analyses of these glasses see reference [2].

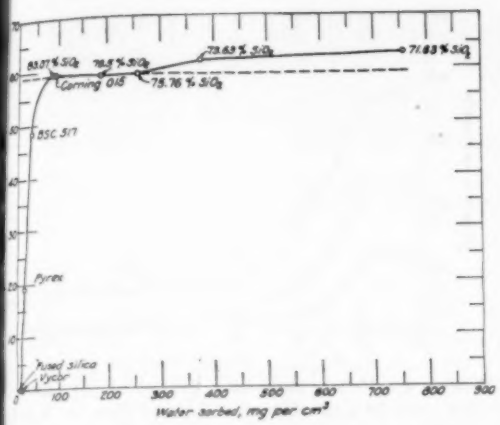


FIGURE 1.—*The water sorbed (hygroscopicity) and accompanying* pH *response of a series of* K_2O-SiO_2 *glasses, Corning 015,* BSC *517, Pyrex, Vycor, and fused silica.*

Values are plotted from columns 4 and 5 of table 1. The broken line indicates the "ideal" voltage response (59 mv) at 25° C.

ated the theoretical pH response. It should not e overlooked that the shift indicated in the pH-sponse—hygroscopicity curve (fig. 1) comes pproximately at the same percentage composi-on at which breaks in the density [11] and hygro-opicity curves [2] have been reported on the me set of glasses.

TABLE 1.—*Hygroscopicity (water sorbed) and* pH *response of* K_2O-SiO_2 *glasses compared with Corning 015 and some glasses of low hygroscopicity*

The pH-response data were obtained below pH 4.5 to avoid the voltage departures which accompany durability shifts at higher pH values. Values in italics are greater than the theoretical]

Glasses		Water sorbed after—		pH response—		Remarks
K_2O	SiO_2	1 hr	2 hr	When prepared	After 24 hr	
Percent	*Percent*	*mg/cm²*	*mg/cm²*	*mv/pH*	*mv/pH*	
28.17	71.83	240	755	*63.0*	*66.7*	Drifting.
26.37	73.63	126	375	*61.4*	*65.5*	Do.
24.24	75.76	102	259	58.9	59.3	Steady.
20.50	79.50	87	186	58.5	58.9	Do.
19.01	80.99	.....	.....	59.3	Failed	Do.
16.93	83.07	46	91	59.3	...do.....	Do.
Corning 015.....		54	94	59.2	59.4	Do.
BSC 517.....		25	36	48.3	50.4	Sluggish.
Pyrex (chemical ware).....		17	22	18.8	19.1	Do.
Vycor.....		14	17	(1)	(1)	.....
Fused silica.....		11	12	(1)	(1)	.....

[1] Developed no definite pH response.

All these electrodes failed in a few days, some after standing for less than 24 hours in distilled water.

Undoubtedly K_2O-SiO_2 glasses of silica content higher than 83 percent would continue to show decreasing hygroscopicity and would follow the pH-response–hygroscopicity curve toward fused silica, the end member of the series.

2. Voltage Departures (Errors) With Increasing pH

Voltage departures were determined over an extended pH range on electrodes prepared from the K_2O-SiO_2 glasses and Corning 015, using the Beckman glass electrode as the reference electrode. If the reference electrode and the experimental electrode had similar pH response, i. e., followed the Nernst equation, the emf would remain constant over the entire pH range. Any deviations from constancy are considered due to errors in pH response of the experimental electrode and are reported in table 2 as voltage departures (errors). The measurements were taken in the buffer sequence, acid to alkaline, followed immediately by the reverse, in order to ascertain the reversibility of the electrodes and to check the effect of their immediate previous history. [12]. The

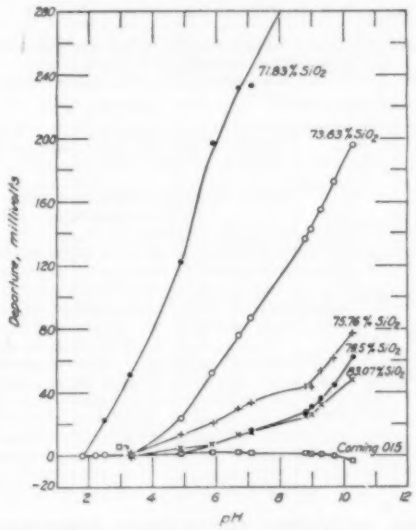


FIGURE 2.—*Voltage departures (errors) of electrodes prepared from a series of* K_2O-SiO_2 *glasses and Corning 015, using the Beckman glass electrode as the reference electrode.*

Values plotted are from table 2 and are the data obtained in the pH sequence, acid to alkaline.

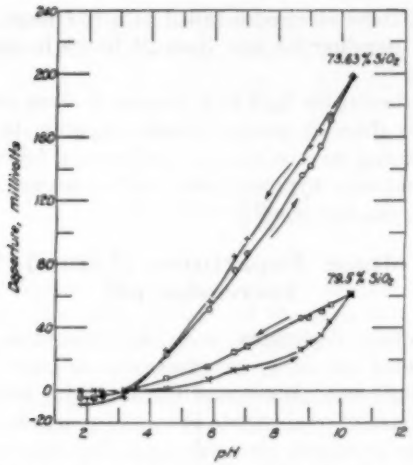


FIGURE 3.—*Voltage departures (errors) of electrodes prepared from two K_2O-SiO_2 glasses.*

These curves are typical and illustrate the irreversibility of pH measurements for the glasses investigated. The values plotted are from table 2.

voltage departures (errors) were very large (fig. 2). The reversibility was poor and greatly affected by the immediate previous environment of the electrode, as shown by the data plotted in figure 3 for glasses of 73.63 and 79.50 percent SiO_2.

TABLE 2.—*Voltage departures (errors) of electrodes prepared from K_2O-SiO_2 glasses of various compositions, using the Beckman glass electrode as the reference electrode*

Readings in row (a) were taken in the order of increasing pH, and those in row (b) were taken immediately in the reverse order

Glass composition			pH value											
K_2O	SiO_2		1.8	2.2	2.5	3.3	4.9	5.9	6.7	7.1	8.8	9.0	9.3	9.7	10.3
%	%		mv	mv	mv	mv	mv	mv	mv	mv	mv	mv	mv	mv	mv
28.17	71.83	(a)	0	....	23	51	121	198	230	233	311	....	345	....	375
		(b)	....	....	....	....	....	....	....	....	....	....	....	....	....
26.37	73.63	(a)	0	0	1	0	23	51	76	87	136	142	155	173	196
		(b)	−9	−5	−4	−4	26	57	85	96	147	155	165	173	196
24.24	75.76	(a)	0	0	0	1	14	21	31	34	43	43	53	62	78
		(b)	−7	−8	−8	−1	2	11	22	32	51	52	60	61	78
20.50	79.50	(a)	0	0	0	0	1	7	13	18	27	31	36	44	62
		(b)	−4	−3	−2	−1	6	16	25	29	46	46	50	55	62
16.93	83.07	(a)	0	0	0	1	5	7	13	14	24	26	32	....	48
		(b)	−16	−14	−14	−7	1	5	6	10	24	....	28	32	48
Corning 015		(a)	0	1	0	1	1	2	2	1	1	1	0	−1	−3
		(b)	2	1	0	0	1	−1	−1	−1	0	0	0	−1	−3

Upon comparing the voltage departures for this series of glasses at any chosen pH values with the percentage compositions, curves are obtained that suggest a sharp change in slope between 74 and 76 percent of SiO_2 (fig. 4). An

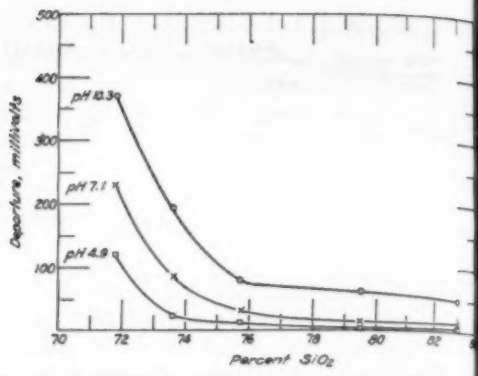


FIGURE 4.—*Voltage departures (errors) at* pH *values* 4.[illegible], 7.1, *and* 10.3 *for electrodes prepared from the* K_2O-SiO_2 *glasses.*

The values plotted are from the data in table 2.

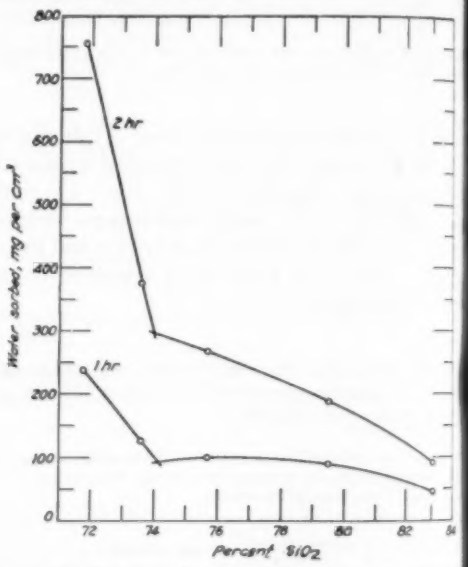


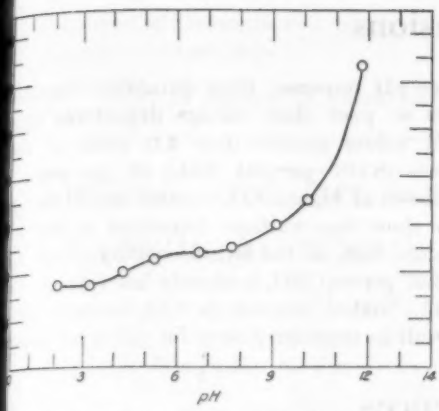
FIGURE 5.—*Water sorbed by K_2O-SiO_2 glasses (hygroscopicity) as a function of the silica content.*

Values are plotted from table 1 for water sorbed during 1-hr and 2-hr period

abrupt change in properties is indicated also by the hygroscopicity-percentage-silica curves shown in figure 5, and by a marked change in density [2, 11].

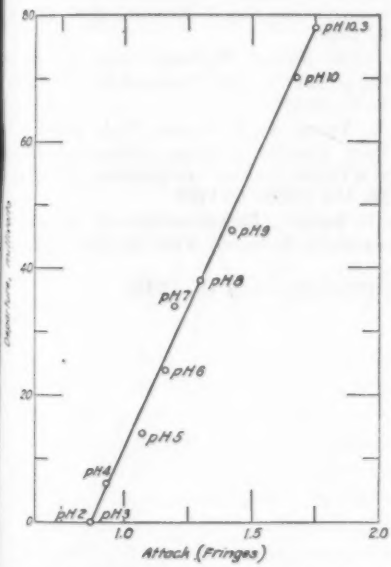
3. Voltage Departure With Reference to Chemical Durability and Sodium Ion Concentration

Voltage departures from the straight-line relation, exhibited by glass electrodes, have generally been interpreted as an equilibrative response to



6.—*Attack*-pH *curve of a potash-silica glass* (K_2O *percent,* SiO_2 *75.76 percent) exposed 15 minutes at C to Britton-Robinson universal buffer mixtures ing the range* pH *2 to* pH *12.*

of the circles does not indicate the probable error of the individual but does emphasize that the data must not be considered highly accurate.



7.—*Comparison of voltage departure with chemical k for a potash-silica glass containing 75.76 percent of and 24.24 percent of* K_2O.

for voltage departure and chemical attack were obtained from figd figure 6, respectively.

ions other than hydrogen [7]. However, for electrodes prepared from Corning 015 and similar glasses it has been demonstrated that the regions of voltage departure have always been accompanied by a shift in the chemical durability of the glass [5, 9]. Conversely, imposed environments, such as hydrofluoric acid solutions, which induce durability shifts in the glass, have been accompanied by voltage departures [5; 1, p. 131].

In order to obtain further evidence on these two interpretations of the voltage departure of glass electrodes, the chemical durability of the glass containing 75.76 percent of SiO_2 was determined by the interferometer method [5, 9; 1, p. 83] over an extended pH range (fig. 6). The values plotted in figure 7 for attack [5] in terms of interference fringes, and the values for voltage departure were obtained by interpolation of the data in figures 6 and 2, respectively. The resulting plot indicates a straight-line relation within reasonable limits.

From the data it becomes obvious that these voltage departures are not attributable to a response to the sodium-ion concentration $[Na^+]$, at least not in accord with the dictates of the straight-line relation. From pH 3.3 to 10.3 the voltage departure was 77 mv (table 2), whereas the change in pNa was only $1.48-1.05=0.43$,[6] or 179 mv per pNa. This voltage response is much greater than the 59 mv per pNa predictable from the Nernst equation. For glasses with poorer durability, such as those of 73.63 and 71.83 percent of SiO_2, this lack of correspondence between pNa and voltage departure is even larger, and the idea of an equilibrative response to $[Na^+]$ by these glasses must be abandoned.[7]

[5] The magnitude of the attack, that is, the thickness of the glass dissolved away, was determined by observing the displacement of the interference fringes when the specimen was placed under a fused silica optical flat.

[6] The buffers of pH 3.3 and pH 10.3 were prepared by the addition of 20 ml and 80 ml of 0.2 *N* NaOH to 100 ml portions of the prepared acid mixture, yielding solutions of $[Na^+]$ equal to 0.033 and 0.088, respectively, or values for $pNa=\log 1/[Na+]$ of 1.48 and 1.05.

[7] Although the evidence strongly indicates a correspondence between the voltage departures and change in the durability of the glass, rather than a response to $[Na^+]$ of the buffers, the following observation should not be overlooked. W. J. Hamer, of this Bureau, points out that an extrapolation of the present data indicates that a glass of composition near 11% K_2O-89% SiO_2 might be expected to show a response to $[Na^+]$ approximating the theoretical 59 mv per pNa. Such a glass would be of interest, as it might serve as an indicator for a metal ion that is absent from the glass itself.

IV. Conclusions

The results of this investigation further support the belief that glasses of high hygroscopicity (water sorption) will always have sensitive pH responses and that changes in the durability of a glass will always be accompanied by voltage departures for an electrode prepared from such a glass.

The K_2O-SiO_2 glasses offer little to recommend them for glass-electrode work. Although their hygroscopicity is high, giving them a very sensitive pH response, their durability characte are so poor that voltage departures appe pH values greater than 4.0, even for the glass (83.07 percent SiO_2) of the series t Glasses of higher SiO_2 content would be exp to show less voltage departure in the al range, but, as the hygroscopicity of the gl 83.07 percent SiO_2 is already less than the Co 015, further increase in SiO_2 content woul result in superior glasses for pH measurem

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rification and Sealing "in Vacuum" of National Bureau of Standards Standard Samples of Hydrocarbons*

Beveridge J. Mair, Domenic J. Termini, Charles B. Willingham, and Frederick D. Rossini

This report describes the procedure and apparatus used in the purification and sealing "in vacuum" of 19 National Bureau of Standards Standard Samples of hydrocarbons, including 9 paraffins, 3 cycloparaffins, and 7 alkylbenzenes.

I. Introduction

ly in 1943, the Technical Advisory Com- of the Petroleum Industry War Council sted the National Bureau of Standards to e hydrocarbons of high purity in its Stand- Samples program. On June 1, 1943, the announced that such work would be started quested the laboratories of the petroleum, r, and chemical industries to submit sugges- as to the compounds most urgently needed, es of the samples, etc. Work on the project ctually begun on July 1, 1943, in the Section hermochemistry and Hydrocarbons in the u's Chemistry Division.

January 10, 1944, announcement was made availability of 15 hydrocarbon compounds ntane, isopentane, each of the five hexanes, hexane, methylcyclopentane, benzene, tolu- ethylbenzene, and each of the three xylenes) ational Bureau of Standards Standard Sam- f hydrocarbons. On December 1, 1944, an ional four compounds (*n*-heptane, 2,2,4-tri- lpentane, methylcyclohexane, and isopropyl- ne), together with a second lot of one of the 15 (toluene), was announced. Three of the compounds (2,2,4-trimethylpentane, methyl- hexane, and toluene) were certified as to re- ve index at seven wavelengths at 20°, 25°, 30° C, by the Bureau's Optical Instruments on, and as to density at 20°, 25°, and 30° C, e Capacity and Density Section, for calibrat- ing refractometers, spectrometers, picnometers, and density balances. One of the latter compounds (2,2,4-trimethylpentane) was certified as to calorimetric heat of combustion, by the Heat Measurements Section, for calibrating apparatus for determining the heating value of gasoline and other liquid fuels.

The present report describes the purification and sealing "in vacuum" of the above mentioned NBS Standard Samples of hydrocarbons.[1]

[1] Information concerning the certification of 2,2,4-trimethylpentane, methylcyclohexane, and toluene for refractive index (by the Bureau's Optical Instruments Section) and density (by the Capacity and Density Section), and of 2,2,4-trimethylpentane for calorimetric heat of combustion (by the Heat Measurements Section) is given in the certificates supplied with those Standard Samples.

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nted before the Division of Petroleum Chemistry of the American Chemical Society, Chicago, Ill., September 1946.

II. Materials and Purification

The materials for the first lots of these 19 NBS Standard Samples of hydrocarbons were obtained as follows:

By gift, the following starting materials were obtained: 2,3-dimethylbutane, from the M. W. Kellogg Co., New York, N. Y., and the Standard Oil Co. (Indiana), Whiting, Ind.; methylcyclopentane, from the Houdry Process Corporation, Marcus Hook, Pa.; cyclohexane, from the Barrett Division of the Allied Chemical & Dye Corporation, New York, N. Y.; *o*-xylene, from the Standard Oil Development Co., Elizabeth, N. J.; isopropylbenzene, from the Atlantic Refining Co., Philadelphia, Pa., through the Technical Advisory Committee of the Petroleum Industry War Council and the Standard Oil Development Co.; *n*-hexane, 2-methylpentane, and 3-methylpentane, from the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

By purchase, the following commercially available starting materials were obtained: *n*-Pentane, isopentane, and 2,2-dimethylbutane, from the Phillips Petroleum Co., Bartlesville, Okla.; *n*-heptane from the Westvaco Chlorine Products Co., New York, N. Y.; 2,2,4-trimethylpentane, from the Rohm & Hass Co., Philadelphia, Pa.; ethylbenzene, *m*-xylene, and *p*-xylene, from the Eastman Kodak Co., Rochester, N. Y.; benzene, from the Jones & Laughlin Steel Corporation, Pittsburgh, Pa.; toluene, from the J. T. Baker Chemical Co., Phillipsburg, N. J.

The starting materials for renewal lots of 15 of the above hydrocarbons were obtained as follows:

By gift, the following starting materials for renewal lots were obtained: Toluene, from the Humble Oil & Refining Co., Houston, Tex.; *o*-xylene, from the Standard Oil Development Co., Elizabeth, N. J.; 2,3-dimethylbutane, from the Phillips Petroleum Co., Bartlesville, Okla.

By purchase, the following starting materials for renewal lots were obtained: *n*-Pentane, isopentane, 2,2-dimethylbutane, *m*-xylene, *p*-xylene, and benzene, from the same sources as the first lots; *n*-hexane, 2-methylpentane, 3-methylpentane, and methylcyclopentane, from the Phillips Petroleum Co.; cyclohexane from the Barrett Division of the Allied Chemical & Dye Corporation; ethylbenzene, from the Dow Chemical Corporation.

The purification to which the above starting materials were subjected was similar to that described in references [1, 2, 3], with reg regular and azeotropic distillation. Benze *p*-xylene were subjected to crystallizatio and *m*-xylene was purified by sulfonati hydrolysis of the sulfonic acids prior to th distillation. The following is a summary purification:

Regular distillation alone was used for tane, isopentane, 2,2-dimethylbutane, *n*-h 2,2,4-trimethylpentane,[2] and isopropylbenz

Both regular distillation and azeotropic d tion were used for *n*-hexane, 2-methylp 3-methylpentane, 2,3-dimethylbutane, met clopentane, cyclohexane, methylcyclohexa uene, ethylbenzene, and *o*-xylene.

Crystallization, followed by filtration th silica gel and by regular distillation, was used purification of the benzene. The crystall was performed as follows: A volume of abo ml of benzene was mixed with 50 ml of eth a cylindrical brass container (5 cm in di and 20 cm in length), which was placed in t ing bath of ice and salt water (temperatur −10° C). With vigorous hand stirring scraping, a thick mush, or slurry, of hydro and alcohol was produced. This slurry wa transferred to the basket of a centrifuge[3] h a jacket cooled to near −10° C with a mix ice and salt water. The centrifuge was op for about 5 minutes, leaving in the basket half of the benzene in crystalline form. crystals were removed from the bask the centrifuge and melted. The purified benzene was washed three times with di water and then filtered through silica gel t move any alcohol and water remaining dis in the hydrocarbon. The total quantity of zene was purified in this way, in 200-ml por

For the crystallization of the *p*-xylene, the apparatus and procedure was used, except the cooling bath was a mixture of water an at 0° C.

In the purification of the starting *m*-xy which contained 5 to 10 percent of *p*-xyl

[2] The small amount of olefinic impurity in this material was rem adsorption with silica gel.

[3] The centrifuge used in this work was a stock model (No. 418) of th national Centrifuge Co., Boston, Mass., altered by them to have a th insulated jacket suitable for containing a refrigerant. The rotating (5 in. in diameter and 2 1/2 in. in height) had a maximum speed of near 3,600 rpm. The wall of the basket was wire cloth, of 325 mes ported by perforated metal.

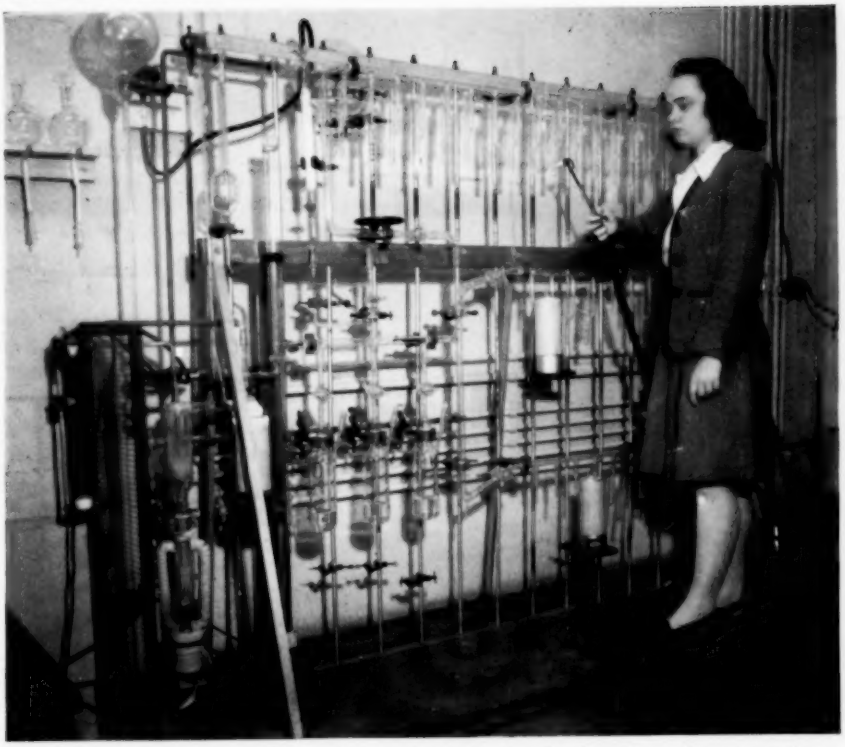

FIGURE 1.—*Apparatus for sealing Standard Samples of hydrocarbons "in vacuum."*

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purity, the bulk of the *p*-xylene was first moved by sulfonation and hydrolysis of the sulnic acids, as follows (see reference 11): A 5-liter rex glass flask with three necks, equipped with stirrer, glass thermometer, and a 500-ml separatory funnel, was placed in a pail of cold water hose temperature was kept below that of the om. A volume of 1,200 ml of the *m*-xylene was ced in the flask, and 1,300 ml of concentrated 6 percent by weight) sulfuric acid was slowly ded through the separatory funnel, while rring, over a period of 3 hours. The temperare of the sulfonation reaction was kept between ° and 45° C by regulating the rate of introducn of acid and by cooling the water surrounding reaction flask. About 30 minutes after all the lfuric acid had been added, 1,100 ml of distilled ter was introduced slowly while stirring. hen the stirrer, separatory funnel, and surrounding water bath were removed. The 5-liter flask ntaining the reaction mixture was placed on a ipod and fitted with an inlet tube for steam and condenser on the outlet leading to a receiver. eam was introduced, and the reaction mixture s brought, with external heating, to a temperare of 125° C, when distillation began. Hydrols occurred slowly at 125° C, but rapidly at 130° 132° C. The distillate of water plus hydrobon was collected in fractions of such volume contained about 50 ml of hydrocarbon. The actions were washed with water and filtered rough silica gel. About 5 percent of the hydrobon material was lost in the process of sulnation and hydrolysis. The purity of selected actions was determined by measuring freezing oints [4], in order to locate the purest material r blending for reprocessing or for the final prodct, if sufficiently pure. As required, the process sulfonation and hydrolysis was repeated on elected blended fractions to improve the purity. dditional amounts of starting *m*-xylene [4] were rocessed as required. One lot of *m*-xylene urified by sulfonation and hydrolysis was further urified by crystallization, using the same appaatus and procedure as for the crystallization of enzene, except that the jacket of the centrifuge as cooled to near −80° C with carbon-dioxide urry.

With the exception o 3-methylpentane, the purity of the final selected standard sample lot of each compound was determined by measuring freezing points, with the apparatus and procedure described in reference [4]. The purity of the 3-methylpentane, which has not yet been crystallized, was estimated by analogy with 2-methylpentane, which was from the same source and similarly purified. The results are summarized in table 1.

TABLE 1.—*Summary of the purity of 19 NBS standard samples of hydrocarbons* [a]

Compound	Standard Sample number	Calculated [b] amount of impurity in the sample
		Mole percent
n-Pentane	201	0.25 ±0.10
	201a	.15 ±0.07
2-Methylbutane (isopentane)	202	.13 ±0.06
	202a	.09 ±0.06
n-Hexane	203	.24 ±0.09
	203a	.10 ±0.05
2-Methylpentane	204	.25 ±0.10
	204a	.16 ±0.08
3-Methylpentane	205	[c](.25 ±0.15)
	205a	[c](.20 ±0.15)
2, 2-Dimethylbutane	206	.12 ±0.05
	206a	.10 ±0.04
2, 3-Dimethylbutane	207	.06 ±0.04
	207a	.11 ±0.06
n-Heptane	216	.10 ±0.05
2, 2, 4-Trimethylpentane	(d, f, g) 217	.12 ±0.05
Methylcyclopentane	208	.25 ±0.09
	208a	.11 ±0.06
Cyclohexane	209	.012±0.007
	209a	.010±0.006
Methylcyclohexane	d, f 218	.36 ±0.18
Benzene	210	.05 ±0.02
	210a	[e]
Toluene	211	.04 ±0.02
	d, f 211 a	.04 ±0.02
Ethylbenzene	212	.20 ±0.07
	212a	[e]
1, 2-Dimethylbenzene (o-xylene)	213	.14 ±0.05
	213a	.010±0.007
1, 3-Dimethylbenzene (m-xylene)	214	.17 ±0.07
	214a	.06 ±0.04
1, 4-Dimethylbenzene (p-xylene)	215	.07 ±0.03
	215a	.06 ±0.03
Isopropylbenzene	220	0.07 ±0.03

[a] Complete details as to prices, sizes of samples, and types of containers in which these Standard Samples are available may be obtained by writing to the National Bureau of Standards.

[b] Except for 3-methylpentane, the amount of impurity was calculated from the freezing point of the actual sample (determined as described in reference [4]) and the values of the freezing point for zero impurity and the cryoscopic constant given in the tables of the American Petroleum Institute Research Project 44 [5].

[c] Estimated by analogy with 2-methylpentane.

[d] In process of determination.

[e] This compound has been certified by the NBS Optical Instruments Section as to refractive index at 20°, 25°, and 30° C, at each of 7 wavelengths.

[f] This compound has been certified by the NBS Capacity and Density Section as to density at 20°, 25°, and 30° C.

[g] This compound has been certified by the NBS Heat Measurements Section as to calorimetric heat of combustion.

[4] Essentially the same process of sulfonation and hydrolysis has been ed in this laboratory to purify 1-methyl-3-ethylbenzene which contained appreciable amount of 1-methyl-4-ethylbenzene as impurity.

III. Apparatus and Procedure for Sealing "In Vacuum"

1. Apparatus

The apparatus for sealing the Standard Samples "in vacuum" is shown in over-all view in figure 1 and consists of the following parts: (a) Vacuum pumps and gage, including a mercury diffusion pump, an oil pump, and a McLeod gage: (*b*) a source of compressed air, with gage to regulate the pressure at about 2 lb/in.^{2} above atmospheric pressure; (c) appropriate refrigerants, including water ice, carbon-dioxide slurry (consisting of a mush, or slurry, of solid carbon dioxide with equal volumes of carbon tetrachloride and chloroform), and liquid air (liquid nitrogen is preferable

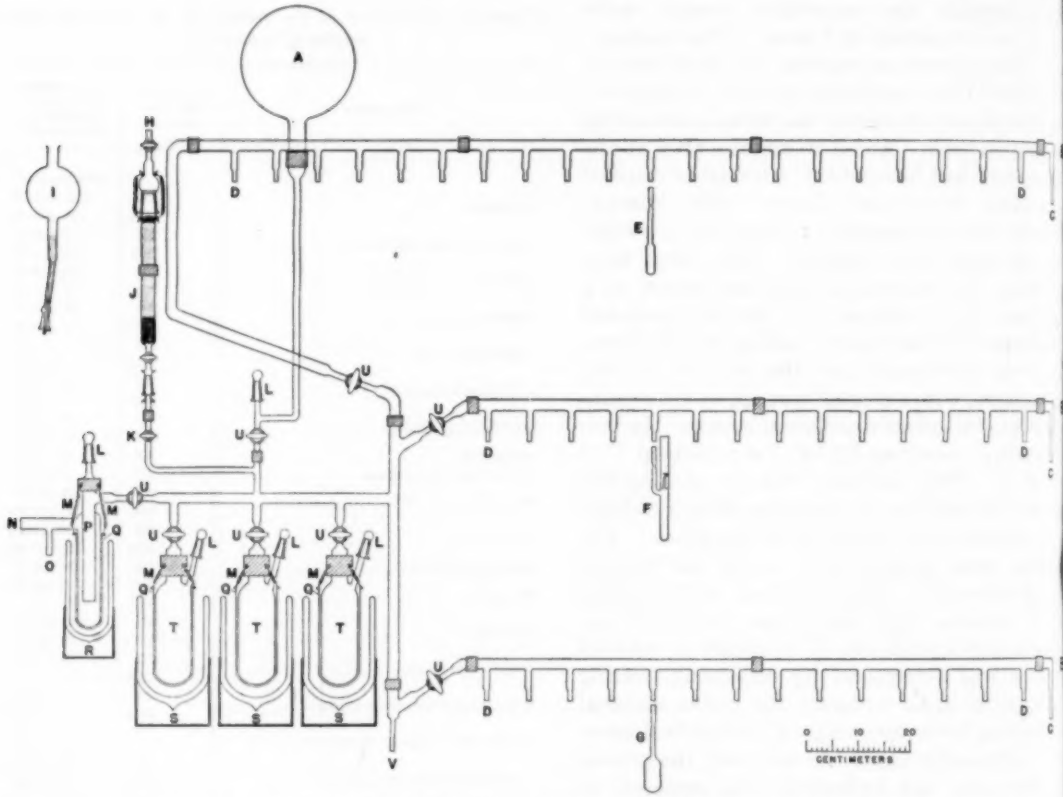

FIGURE 2.—*Manifold system and accessory parts for sealing hydrocarbons "in vacuum."*

A, gas reservoir, with capacity of 5 liters.

B, three branches of the manifold system.

C, outlets, sealed when hydrocarbon is in the system, but opened for use of the glass blower when empty ampoules are being sealed to the manifold.

D, connections to which empty ampoules are sealed.

E, ampoule (plain, with capacity of 5 ml), before being sealed in position.

F, ampoule (with internal vacuum break-off tip, with capacity of 8 ml), before being sealed in position.

G, ampoule (plain, with capacity of 25 ml), before being sealed in position.

H, connection to source of compressed air at a pressure of about 2 lb/in.^{2} above atmospheric pressure.

I, one of three filling tubes (containing silica gel in the shaded portion), which fit on reservoirs *T* at *L* at the time of introducing the hydrocarbon into the reservoirs.

J, tube containing (in order from the outer end) anhydrous magnesium perchlorate and phosphorus pentoxide, separated by layers of dry asbestos, for removing water vapor from the air introduced into the system.

K, stopcock, with oblique bore 3½ mm in diameter, ground for high vacuum.

L, standard ground joints, 14/35, with closed caps.

M, expansion springs, made of bronze wire.

N, connection to the mercury diffusion pump.

O, connection to the McLeod gage.

P, trap, refrigerated with liquid air.

Q, shields on each of the three reservoirs, *T*, and on the trap, *P*, made of thin brass, for protection from the refrigerant.

R, vacuum-jacketed vessel, Pyrex glass, with capacity of 1 pint, for containing liquid air.

S, vacuum-jacketed vessels, Pyrex glass, with capacity of 1/2 gallon, for containing the appropriate refrigerant.

T, reservoirs for the purified hydrocarbon material, with capacity of 500 ml.

U, stopcocks, with oblique bore 7 mm in diameter, ground for high vacuum.

V, outlet for drainage, sealed closed when hydrocarbon is in the system.

available); (d) manifold system and accessory parts, the details of which are shown in figure 2. Details of the several glass ampoules used in this work are shown in figure 3.

2. Procedure

(a) Preparing the apparatus

The apparatus is prepared as shown in figure 2, but with the vessels, R and S, the shields, Q, and the drying tube, J, not yet in position. The ground joints, L (including both male and female parts), and the stopcocks, K and U (including plug and barrel), and the tubing adjacent to it, are cleaned with a cotton swab and with a pipe cleaner, using three fresh portions of carbon tetrachloride as washing solvent. Carbon tetrachloride is introduced into the reservoirs, T, glass-insulated electric heaters [5] are placed in position on the lower part of the reservoirs, and the solvent is boiled at atmospheric pressure. By proper

[5] Glascol Apparatus Co., Terre Haute, Ind.

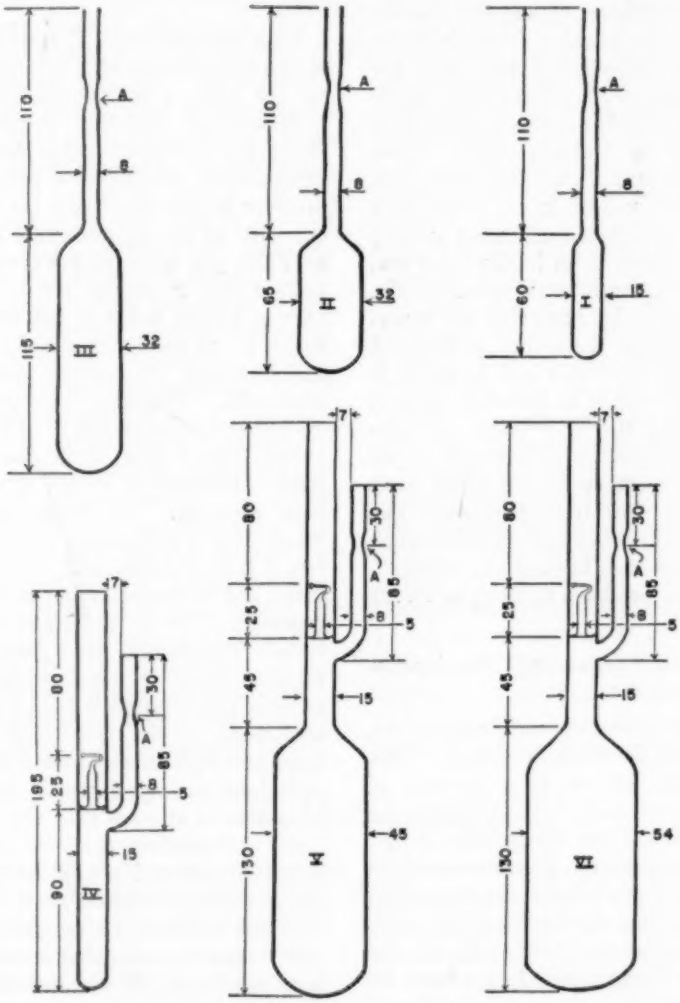

FIGURE 3.—*Glass ampoules used for containing hydrocarbons.*

The ampoules are all made of Pyrex glass. I, Plain ampoule, with capacity of 5 ml; II, plain ampoule, with capacity of 25 ml; III, plain ampoule, with capacity of 50 ml; IV, ampoule with internal vacuum break-off tip, with capacity of 8 ml (taken from drawing A-1626 of the Consolidated Engineering Corporation, Pasadena, Calif.); V, similar to IV, but with a capacity of 135 ml; VI, similar to IV, but with a capacity of 200 ml. *A* indicates a thickened wall at the constriction, to facilitate sealing off "in vacuum."

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manipulation of the various stopcocks, solvent is caused to distill and reflux through all parts of the manifold system. After the solvent is cooled it is removed through outlet V and syphoned out of the trap and reservoirs. The above cleaning process is repeated, with fresh solvent, three times. After liquid solvent from the last refluxing has been withdrawn, all parts of the system are thoroughly flushed with air to remove solvent vapors. The ground joints and stopcocks are lubricated, using the minimum amount of grease (Apiezon L in winter and Apiezon N in summer). The drying tube, J, the metal shields, Q, and the vessels, R and S, are placed in the position shown in figure 2. Ampoules of the desired size and type are sealed to the connecting tubes. The outlet tubes, C, used for blowing during the operation of sealing on the ampoules, and the drainage outlet, V, are closed by fusing. The trap, P, is refrigerated with liquid air. The entire system is evacuated and tested for pinholes. Pinholes are readily located with a spark tester except those in the inner seal of the ampoules having an internal break-off tip. Pinholes here are located by observing the movement of a drop of water at the end of an inverted U-tube, of 2-mm bore, the other end of which is connected with clean rubber to the open arm of the ampoule containing the inner seal.[6] All pinholes must be sealed closed, or, if they are in an inaccessible place in an ampoule, the latter must be replaced with one free from pinholes. The system is ready for the introduction of hydrocarbon when all pinholes have been located and repaired, and when the pressure has been reduced to 0.0001 mm Hg or lower.

(b) Introducing and "degassing" the hydrocarbon

All the stopcocks in the system are closed except the stopcock to one of the three reservoirs. This reservoir is filled with dry air to a pressure of about 2 lb/in.^{2} above atmospheric pressure by opening the stopcocks on the drying tube J and stopcock K. The ground cap on this reservoir is removed, and, while dry air is issuing from the reservoir, the filling tube, I, (freshly filled with silica gel) is placed on the reservoirs at L. At the same time that the filling tube, I, is placed in position, the stopcock to the reservoir is closed. In a similar manner, the other reservoirs are fitted with filling tubes. The drying tube, J, is closed off from the system, and the portion of glass tub ing bounded by the stopcock, K, and the eigh stopcocks, U, is evacuated. Hydrocarbon (pref erably cooled to 0°C) is introduced into the filling tubes, the stopcocks, U, to the reservoirs ar opened, and the liquid drawn into them by par tially and momentarily opening the stopcock, U to the evacuated reservoir, A. After all the hydro carbon has been introduced into the reservoirs, th filling tubes are removed and replaced with caps L, using the same procedure described for th original substitution of the caps with the filling tubes.

With the reservoirs, T, open to the gas reservoir A, the hydrocarbon in T is refrigerated with liquid air (or with a carbon-dioxide slurry for thos hydrocarbons freezing above about −60°C). When the hydrocarbon has become solid, and its temperature reduced to a point where the vapor pressure is not significant (as determined by the quantity of the hydrocarbon required to fill the available gas space at the given pressure), which temperature is usually 160 to 200° C below the normal boiling point of the compound, the stop cocks, U, on the reservoirs, T, are closed, and the gas reservoir, A, and its connecting lines, are evacuated. The gas reservoir, A, is repeatedly opened to the reservoirs, T (still at the low temper ature), closed from them, and then evacuated until a pressure of 0.0001 mm Hg or lower has been attained. The hydrocarbon is allowed to warm (if it is crystalline, only until it has melted but if it is a glassy solid, to near room temper ture), and the refrigeration and evacuation process repeated. Two refrigerations and evacuations are usually sufficient if the hydrocarbon crystallizes whereas three or more refrigerations and evac uations are required if the hydrocarbon does not crystallize in the reservoirs. In the warming operation, it is important to have the hydrocarbon melt from the top down, in order to prevent the formation of stresses that will break the reservoir if the hydrocarbon at the bottom of the reservoir is melted before the solid at the top has had an opportunity to release itself from solid contact with the walls of the reservoir. This melting is safely done by removing most of the refrigerant from the vessel, S, and lowering the vessel until the level of hydrocarbon in T is 2 or 3 cm above the top of the vessel, S. When about half of the hydrocarbon has been melted, downward from the top, vessel S is withdrawn, and the reservoirs are

[6] This simple test was suggested by A. F. Forziati, of this laboratory.

surrounded with water at room temperature to expedite the melting.

(c) Filling and sealing the ampoules

The hydrocarbon is transferred from the reservoirs, T, through the vapor phase at room temperature to the individual ampoules. During this operation, the stopcocks to the trap, P, the drying tube, J, and the gas reservoir, A, are closed, and the stopcocks on the reservoirs, T, and those leading to the branches of the manifold, B, are open. The reservoir, T, is surrounded with water at room temperature, the first ampoule in one of the branches of the manifold is cooled with an appropriate refrigerant (usually carbon-dioxide slurry, but see below), and the hydrocarbon passes as vapor through the line at room temperature from the reservoir to the ampoule. Occasionally, the transfer of hydrocarbon is blocked by the accumulation in the connecting lines of a small amount of air that was not completely removed from the hydrocarbon during the degassing operation. To remove this air, the stopcocks on the reservoirs are closed, the hydrocarbon in the ampoule is cooled to the temperature of liquid air (or to the temperature of carbon-dioxide slurry if the hydrocarbon has a sufficiently low vapor pressure), and the manifold lines are connected to the source of high vacuum. This secondary degassing operation may be repeated as necessary. When the desired quantity of hydrocarbon has been collected in the given ampoule, the stopcock on the given branch of the manifold is closed, and the hydrocarbon vapor remaining in that branch of the manifold is condensed into the ampoule. This ampoule, protected with a close-fitting metal shield, is refrigerated with liquid air (if available, liquid nitrogen is preferable), and is sealed off at the constriction. If the hydrocarbon has a sufficiently low vapor pressure, carbon-dioxide slurry may be used as the refrigerant in the last-named operation. With the apparatus described, it is possible to have three ampoules, one on each of the three branches of the manifold, being filled simultaneously.

When all the ampoules on the manifold have been sealed off and hydrocarbon still remains in the reservoirs to be transferred, the stopcocks to the reservoirs and to the branches of the manifold are closed, the connecting tubes are cut off as shown at D in figure 2, and clean empty ampoules of the desired type and size are sealed on. The manifold system and the ampoules are evacuated, all pinholes are repaired or removed, and the operation of filling and sealing of the individual ampoules is performed as before.

For hydrocarbons such as benzene, *p*-xylene, cyclohexane, and *o*-xylene, which freeze at temperatures above that of the carbon-dioxide slurry, some modification is necessary in the procedure of transferring hydrocarbon from the reservoirs to the ampoules, in order to control the quantity delivered to each ampoule. If carbon-dioxide slurry is used as the refrigerant the hydrocarbon will condense as solid in the ampoule, and it is necessary at appropriate intervals to melt the hydrocarbon to ascertain its quantity, in terms of a measured volume at a given temperature. Three or more such meltings may be required to adjust the quantity in the ampoule within the desired limits. An alternate procedure is to let the refrigerant around the ampoule be one whose temperature is above the freezing point of the given hydrocarbon, so that the latter is condensed as liquid in the ampoule. For the latter procedure, appropriate refrigerants would be ice and water at 0° C for *o*-xylene, water at 7° C for benzene and cyclohexane, and water at 14° C for *p*-xylene.

IV. Discussion

The foregoing apparatus and procedure for sealing "in vacuum" is satisfactory for hydrocarbons having normal boiling points below about 170° C and freezing points below room temperature. The rate of transfer through the vapor phase at room temperature of hydrocarbons normally boiling very much above 170° C becomes almost impracticably slow, however, and a different apparatus has been designed and is being assembled to handle hydrocarbons having normal boiling points above about 170° C, with freezing points either below or above room temperature [6].

For olefin hydrocarbons, the final drying of the hydrocarbon by filtration through silica gel may be used only if such contact with silica gel can be done in such a short time and at a sufficiently low temperature as not to affect the purity of the material. Normally, for olefin hydrocarbons, the filtration through silica gel should be omitted and a different method used to remove the minute

amount of water and oxidation products from the purified material before its introduction into the reservoirs of the apparatus.

The apparatus and procedure described in section III of this report have also been used, since September 1, 1944, to seal [7] "in vacuum" approximately 200 ampoules, each of over 70 hydrocarbons prepared as Standard Samples of hydrocarbons in the cooperative program of the American Petroleum Institute and the National Bureau of Standards on hydrocarbons for spectrometer calibration. Details of this work are given in references [7, 8, 9, 10]. This cooperative program was organized by the API Research Project 46 Committee on Hydrocarbons for Spectrometer Calibration (W. J. Sweeney, chairman).

For the benefit of those laboratories that do not already have an established procedure for transferring Standard Samples of hydrocarbons "in vacuum," there is attached an appendix to this report, which gives a description of the apparatus and procedure used for this purpose for C_8 and higher hydrocarbons by the Hydrocarbon Standard Samples Laboratory at the National Bureau of Standards.

[7] Thomas E. Eble, now with the United States Food and Drug Administration, assisted in this work. The operations of sealing "in vacuum" are currently being performed by Beryl A. Gaffney and Audrey H. Hull, of this laboratory.

Grateful acknowledgment is made to the organizations and individuals listed in section II of this report for their contributions of material for use in this work.

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VI. Appendix.—Apparatus and Procedure for Transferring Standard Samples of Hydrocarbons "In Vacuum"

1. Introduction

For the benefit of those laboratories that do not already have an established procedure for transferring "in vacuum" Standard Samples of hydrocarbons, there is presented here a description of the apparatus and procedure used for this purpose for C_8 and higher compounds in the Hydrocarbon Standard Samples Laboratory at the National Bureau of Standards.

2. Method

The main glass ampoule containing the hydrocarbon, "sealed in vacuum" back of an internal vacuum "break-off" tip, is sealed to a glass manifold to which are also sealed the required number of empty auxiliary ampoules to which the hydrocarbon is to be transferred. The entire system is evacuated. The "break-off" tip is broken by means of an electromagnetic hammer previously installed above the main glass ampoule containing the hydrocarbon. The appropriate amount of hydrocarbon is transferred to the first auxiliary ampoule by refrigerating the latter and permitting the transfer to take place through the vapor phase at room temperature. The main ampoule is re-frigerated, and the first auxiliary ampoule is sealed off. The operations are repeated for each auxiliary ampoule.

3. Apparatus

(a) Vacuum system

This system must be capable of producing and measuring pressure of 0.0001 mm Hg and lower. (A suitable system may consist of a mercury or oil vapor diffusion

pump backed by an appropriate mechanical oil pump, for producing the required low pressure, and a McLeod gage for measuring the low pressure.) For lubricating the ground joints and stopcocks in the high-vacuum system, Apiezon grease *L* may be used in winter and Apiezon grease *N* in summer.

(b) Refrigerant

For hydrocarbons normally boiling below about 80° C, liquid air or liquid nitrogen may be used as the refrigerant. If liquid air is used, each ampoule so refrigerated should be provided with a closely fitting thin-metal cylinder for protection in case of breakage.) For hydrocarbons normally boiling above about 80° C, the refrigerant may consist of a slush, or slurry, of solid carbon dioxide in a 50-50 mixture of chloroform and carbon tetrachloride. For the ampoules, the refrigerants may be contained in cylindrical vacuum-jacketed vessels of about 1-pint capacity.

(c) Manifold system

This assembly is shown in figure 4, as follows: *A*, connection to the high-vacuum system; *B*, standard ground joint and cap, 14/35; *C*, liquid-air or liquid-nitrogen trap, with closely fitting thin-metal protecting tube if liquid air is used; *D*, stopcock, with 3 1/2-mm oblique bore, ground for high vacuum; *E*, main horizontal tube of manifold; *F*, solenoid, about 1,200 ampere turns (a solenoid for this purpose suitable for use directly on 110-volt alternating current, may be made by winding No. 30 AWG copper wire, enameled and single silk covered, in a layer 1.5 cm in thickness on a Bakelite tube 5 cm in length and about 1.8 cm in inside and 2.3 cm in outside diameter.); *G*, connection to main ampoule containing the standard sample (see note (a) below); *H*, iron (mild annealed steel) rod incased in glass (a suitable rod may be 5/16 in. in diameter and 1 1/2 in. long, with rounded ends, fitting inside glass tubing 10 mm in outside diameter with standard wall thickness. The ends of the glass case should be heavily thickened; *I*, main glass ampoule containing Standard Sample; thin-metal protecting tube should be provided if liquid air is to be used; J_1, J_2, J_3, . . . , J_n, connections to auxiliary ampoules; K_1, K_2, K_3, . . . , K_n, auxiliary ampoules; these may be plain or have an internal vacuum break-off tip, as shown; thin metal protecting tubes should be provided if liquid air is to be used; L_1, L_2, L_3, . . . , L_n, place where the auxiliary ampoules are sealed off after filling; *M*, outlet for attaching rubber tubing for blowing glass; outlet is sealed off after all auxiliary ampoules are attached.

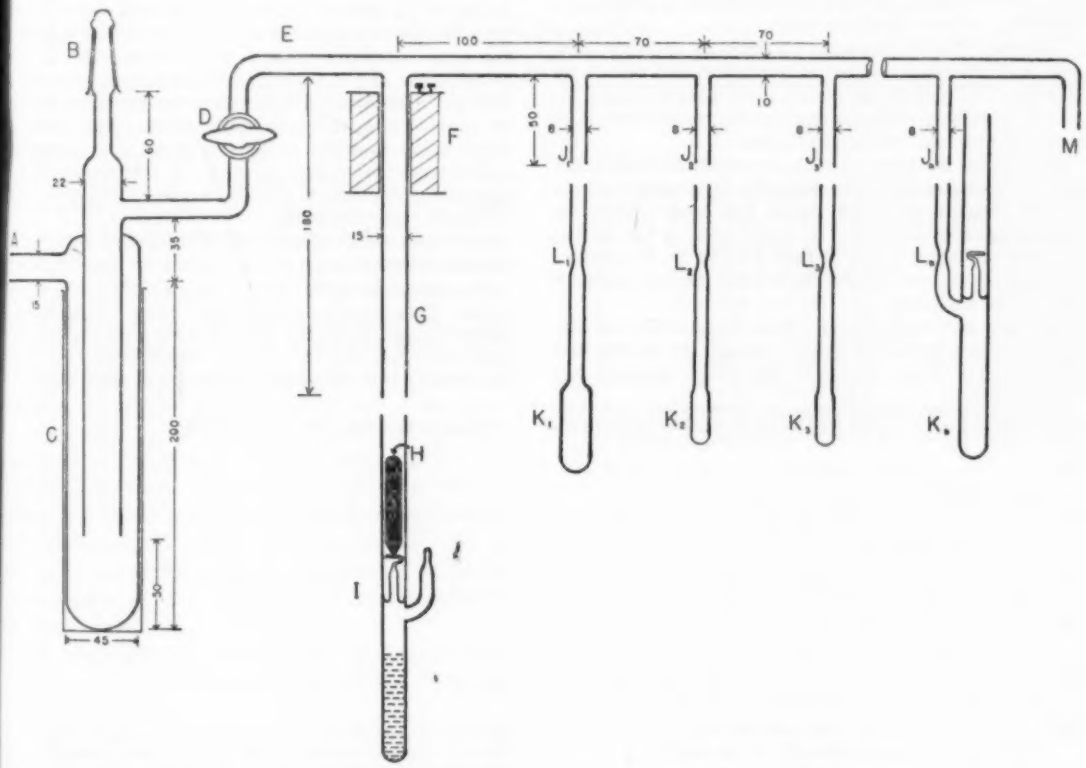

FIGURE 4.—*Apparatus for transferring Standard Samples of hydrocarbons "in vacuum".*

See text in appendix for details. All dimensions in millimeters. Glass is Pyrex.

4. Procedure

The manifold system is prepared as shown in figure 4. The connecting tubes, G (see footnote "a"), J_1, J_2, J_3, . . . , J_n, are cut off to the lengths indicated. The ground joint, A, (including both male and female parts), and the stopcock, D, (including plug and barrel and the tubing adjacent to it), are cleaned with carbon tetrachloride, using a pipe cleaner with cotton swab and three fresh portions of solvent. To remove traces of stopcock lubricant that may be in the tubing near the stopcock, the unlubricated plug of the stopcock is placed in the open position, suction is applied at A, and fresh liquid solvent is drawn into the trap, C, from a beaker of the solvent held around connecting tube G, with the other connecting tubes being temporarily stoppered with clean corks. The solvent is then withdrawn from the trap, C, and vapors of the solvent are removed from the system by flushing with air. The ground joint, A, and the stopcock, D, are then lubricated, using the minimum amount of Apiezon grease L or N.

The glass incased iron rod, H, is placed inside the main ampoule, I, as shown in the illustration. Ampoule I is sealed to connecting tube G. The auxiliary ampoules, K_1, K_2, K_3, . . ., K_n, are sealed to the connecting tubes, J_1, J_2, J_3, . . ., J_n, respectively. The outlet, M, used for blowing during the operations of sealing on the ampoules, is then closed by fusing.

The trap, C, is refrigerated with liquid air or liquid nitrogen, and the entire system is evacuated and tested for pinholes.[3] If pinholes are found, these must be sealed, or, if in an inaccessible place in an ampoule, the latter must be replaced with one free from pinholes.

Evacuation is continued until the pressure is reduced to below 0.0001 mm Hg. The stopcock, D, is closed and the internal vacuum break-off tip in I is broken with the electromagnetic hammer. In most cases, a fall of the hammer through a height of from 5 to 10 cm is sufficient to break the tip, but in some cases a fall through about 20 cm may be necessary.

The first auxiliary ampoule, K_1, is refrigerated and the hydrocarbon is permitted to pass through the vapor phase from I to K_1. When nearly the appropriate quantity has been transferred to K_1, the passage of hydrocarbon to K_1 is halted by refrigerating the main ampoule, I, and the ampoule K_1 is sealed off at L_1. See note (b).

The remaining auxiliary ampoules, K_2, K_3, . . ., K_n, are than sealed off in order.

[3] For the method of locating pinholes in the internal vacuum break-off tip of the special ampoules, see section III-2-a of the preceding part of this report.

5. Discussion

For a modification of the apparatus and procedure when many volatile samples are to be transferred, see note (c).

6. Notes

(a) If the main ampoule, I, containing the Standard Sample, is made of Pyrex red glass (No. 2,280), a short length of tubing of 15-mm outside diameter, consisting of 50 mm of ordinary Pyrex clear glass (No. 774) joined to 10 mm of Pyrex uranium glass (No. 332) joined to 50 mm Pyrex red glass (No. 2,280) (which piece of tubing is obtainable on request from the National Bureau of Standards), is first sealed to connecting tube G, with the Pyrex red glass end of the added tube being free to receive the Pyrex red-glass ampoule. The same connecting tube may be used over and over again.

(b) For refrigeration at the time of sealing off the ampoules, liquid air or liquid nitrogen is recommended to be used for those hydrocarbons normally boiling below about 80° C, and a slush, or slurry, of solid carbon dioxide (in a 50-50 mixture of chloroform and carbon tetrachloride) for those normally boiling above about 80° C. For refrigeration of the auxiliary ampoules during the time of transfer of hydrocarbon, the slush of carbon dioxide may be used, except when the hydrocarbon solidifies at this temperature, in which case water at 0° C or appropriate higher temperature may be used. Before sealing off, the ampoules, however, a change to the appropriate lower refrigerant must be made.

(c) When many volatile samples in larger amounts are to be transferred, time may be saved by inserting in the main tube, E, between G and J_1, a second stopcock similar to D. This second stopcock can be used to isolate the main ampoule, I, at the time of sealing off the auxiliary ampoules, J_1, J_2, J_3, . . ., J_n, which procedure makes unnecessary the refrigeration of the main ampoule, I.

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Thermal-Expansion Stresses in Reinforced Plastics [1]

By Philip S. Turner [2]

Failure of adhesive bonds is attributed to boundary stress concentrations. An analysis of the causes of internal-stress concentrations in rigid adhesive layers leads to the conclusion that stress concentrations can be eliminated in many cases by matching the coefficients of thermal expansion of the component parts. A stress-equilibrium formula for calculating the thermal-expansion coefficients of mixtures involves the density, modulus of elasticity, coefficient of thermal expansion, and proportion by weight of the ingredients. Illustrations of the application of the derived formula include lead-antimony and beryllium-aluminum mixtures, phenol-formaldehyde resin and glass-fiber mixtures, and plastic plywoods. The thermal-expansion coefficients of a number of pure and reinforced plastics are reported. Bonds obtained when thermal coefficients are matched are stable over a wide temperature range.

I. Introduction

This report describes a method of compounding plastic, or other mixture or compositions, to provide a material having a predetermined desired coefficient of thermal expansion. In the preparation of plastics heretofore it has been found practically impossible to produce a satisfactory bond between a plastic and a metal facing or other metal reinforcement. This is largely due to the difference in coefficients of expansion of the materials; the plastics have relatively high coefficients of expansion as compared with those of metals. Because of the differential expansion, forces created upon changes in temperatures have been such as to prevent a satisfactory bond being obtained between metals and plastics except where plastics of a flexible rubber-like, or gummy type are used. Even in the bonding of foils of tin, lead, aluminum, etc., to cardboard or paper for containers, only gummy or tacky plastics have been used.

The problem of obtaining bonds between plastics or other adhesives and various materials

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[1] The experimental work on this project was sponsored by and conducted with the financial assistance of the National Advisory Committee for Aeronautics, upon the recommendation of their Subcommittee on Wood and Plastics for Aircraft.

[2] Deceased.

is considered as being substantially the same as that of removing or eliminating concentrated stresses at the boundaries. If internal-stress concentrations can be removed, the full strength of the adhesive can be developed to resist external loads.

Bonds produced by adhesives can be divided into two general classes: the rubbery or yielding bond and the rigid bond. In the first category are found most thermoplastic cements, rubber cements, and combinations of thin rubber layers and cements. Adhesives of this class have been found to provide durable bonds between dissimilar materials at moderate temperatures. The rigid or high modulus bond has generally been found unsatisfactory for such applications. A possible exception is found in the use of cold-setting cements of the phenol-formaldehyde and urea-formaldehyde types. The advantages of the first class over the second disappear at reduced temperatures where the adhesive loses its ability to eliminate stress concentrations by yielding with the dimensional changes of the materials bonded. The rigid bond is superior for many purposes to the yielding bond, if it can be obtained, because it produces a stronger and less-yielding product. For composite structural materials subjected to extreme temperature changes a stable rigid bond is imperative.

In attempting to bond various materials together, it has been found that materials having widely different coefficients of expansion cannot be bonded with any rigid cement available. Certain thermoplastic adhesives produce satisfactory bonds at ordinary temperatures, but fail at low temperatures when the bond becomes rigid and is no longer able to yield to changes in dimension of the materials bonded. Certain rubber cements fall into the classification of bonds which are soft enough to yield with changes in dimensions. These yielding bonds, however, do not produce the rigidity required for structural applications and fail at low temperatures for the same reason that rigid plastic bonds fail at ordinary temperatures; namely, difference in rates of expansion and contraction with changes in temperature.

These failures are caused by stresses resulting from differential expansion or contraction. These forces can be reduced by one or more of the following factors.

II. Effect of Various Factors on Bond Strengths

An analysis of the factors responsible for the production of stress concentrations in a rigid bond must include the following:

1. The thickness of the materials bonded.
2. The thickness of the adhesive layer.
3. The modulus of elasticity of all components.
4. Changes in dimensions with changes in moisture content for all materials.
5. Changes in temperature to be encountered in service.
6. Coefficients of linear thermal expansion of all materials.
7. Pressure of application.

1. Thickness of Materials Bonded

It is evident that if the thickness of the materials bonded approaches zero, stresses set up by any other combination of factors must also approach zero. Accordingly, it has been found possible to bond thin metal foils to other materials. A method of eliminating stresses by this means would, however, have very limited practical application. This stress-reducing factor is utilized in the production of mechanical mixtures of materials of microscopic size or in the form of fine filaments, which are incompatible on a larger scale.

2. Thickness of Adhesive

In bonding two pieces of the same material the stresses set up in the bond as the result of restrained dimensional changes in the bonding material would be proportional to the thickness of the bond. It has long been recognized that thin adhesive layers produce stronger bonds than thicker ones.

3. Modulus of Elasticity

If the modulus of elasticity of any one of two adjacent materials is zero, the stresses set up between them must be zero. This is essentially achieved by bonds which yield readily and offer little resistance to static loads whether produced internally or externally.

4. Moisture Content

The problem of bonding materials having different dimensional stability with changes in ative humidity can be reduced, if not eliminated, he surface of the combination is impervious to isture. At the time of bonding or at the end he bonding operation the material or materials sitive to changes in humidity can be made to tain the normal amount of water present der average conditions. No completely satisory solution to this aspect of bonding has been nd.

5. Temperature

Changes in temperature cannot be eliminated any practical application. For cold-setting nol-formaldehyde and urea-formaldehyde ce-nts the effect of temperature changes is imized by bonding at temperatures close to se encountered in service.

6. Thermal Expansion

From the standpoint of the thermal stresses oduced, the problem of bonding two different terials becomes identical with the problem of ding two pieces of the same material, provided coefficients of thermal expansion of the two terials are the same. A further reduction in sses can be achieved if the bonding agent has same coefficient of thermal expansion as the terials bonded. A bond between materials ving different coefficients of expansion would e to withstand the shear stresses produced by differential expansion or contraction expe-nced within the range of temperatures en-ntered. Bonds can sometimes be maintained the materials bonded are thin enough to permit relief of stresses by bending or warping, either which is undesirable. The bonding strength hibited by a particular adhesive is the addi-nal load which, added to the internal concen-ted stresses, is sufficient to disrupt the material. In some cases this additional load is zero and the materials are said not to bond.

7. Pressure of Application

When two materials are bonded together at high pressures, strains are produced at the bond when the pressure is released. This strain is proportional to the ratio of the moduli of elasticity of the two components. The lowest pressure feasible should be used to produce bonds with the lowest internal strains.

The logical conclusion to be drawn from the foregoing discussion is that stable rigid bonds are possible over a wide range of temperatures if the thermal-expansion coefficients of the component parts are matched. An example of the results to be expected is furnished by the combination of concrete and steel which individually have practically equal coefficients of thermal expansion and contraction. It is noted that certain proportions of cement, sand, and stone produce optimum results.

Various methods have been used in other fields to predetermine the thermal-expansion coefficients of mixtures, such as alloys, glasses, etc. Some of these methods appear to work satisfactorily in limited applications. Notable among these are weighted averages based on the thermal-expansion coefficients of the components and their proportions either by weight or by volume. These methods do not, however, give satisfactory results for plastic compositions.

It seems reasonable to expect that the coefficient of thermal expansion of a mixture is a function of the relative compressibilities, as well as the thermal expansion coefficients and the proportions of the components. In the following section a formula for the coefficient of thermal expansion for a mixture is obtained which, although not derived rigorously (according to the theory of elasticity), does take into account the relative compressibilities of the components.

III. Development of a Formula for Calculating Coefficients of Thermal Expansion of Mixtures

If it is considered that an internal stress system a mixture is such that the stresses are nowhere fficient to disrupt the material, the sum of the ternal forces can be equated to zero and an expression for the thermal-expansion coefficient of the mixture is obtained. When small particles or fine filaments are incorporated into a mixture, the small dimensions appear to permit combinations

of materials which would be incompatible on a larger scale.

The derivation of the resulting volume thermal coefficient of a mixture follows. The symbols used are:

α=coefficient of linear thermal expansion
β=coefficient of cubical thermal expansion
K=bulk modulus=1/bulk compressibility
d=density
P=fraction or percent by weight
V=volume
ΔT=temperature difference
S=stress.
Subscripts i and r refer respectively to the property of the ith component and of the resultant mixture.

If it is assumed that each component in the mixture is constrained to change dimensions with temperature changes at the same rate as the aggregate and that shear deformation is negligible, the stresses acting on the particles of the various components will be

$$S_i=(\beta_r-\beta_i)\Delta TK_i, \qquad (1)$$

as the stress is given by the product of volume strain and bulk modulus. The resultant of the forces acting on any cross section of the mixture must vanish. Therefore,

$$S_1A_1+S_2A_2+ \ . \ . \ . \ +S_nA_n=0, \qquad (2)$$

where there are n components and the A's refer to the parts of the cross-sectional area formed by the various components. However, in a homogeneous mixture the relative areas formed in the cross section by the different components are proportional to their relative volumes. Therefore, it follows from equation 2 that

$$S_1V_1+S_2V_2+ \ . \ . \ . \ +S_nV_n=0. \qquad (3)$$

Substitution for S from equation 1 in equation 3 then yields

$$(\beta_r-\beta_1)\Delta TV_1K_1+(\beta_r-\beta_2)\Delta TV_2K_2+ \ . \ . \ . \ . \ +$$
$$(\beta_r-\beta_n)\Delta TV_nK_n=0. \qquad (4)$$

As

$$V_1+V_2+ \ . \ . \ . \ . \ +V_n=V_r, \ V_i=\frac{P_id_rV_r}{d_i}$$

which can be substituted for V in equation 4. Also, as ΔT, d_r, and V_r are common factors, they can be eliminated from each term of the expression. Solving for β_r, the following expression is obtained:

$$\beta_r=\frac{\frac{\beta_1P_1K_1}{d_1}+\frac{\beta_2P_2K_2}{d_2}+ \ . \ . \ . \ . \ +\frac{\beta_nP_nK_n}{d_n}}{\frac{P_1K_1}{d_1}+\frac{P_2K_2}{d_2}+ \ . \ . \ . \ . \ +\frac{P_nK_n}{d_n}}.$$

As the coefficient of linear thermal expansion directly proportional to the cubical coefficie α can be substituted wherever β appears with following

$$\alpha_r=\frac{\frac{\alpha_1P_1K_1}{d_1}+\frac{\alpha_2P_2K_2}{d_2}+ \ . \ . \ . \ . \ +\frac{\alpha_nP_nK_n}{d_n}}{\frac{P_1K_1}{d_1}+\frac{P_2K_2}{d_2}+ \ . \ . \ . \ . \ +\frac{P_nK_n}{d_n}}.$$

It is apparent by inspection that equation based on stress equilibrium reduces to a perce age by volume calculation if the ingredients h

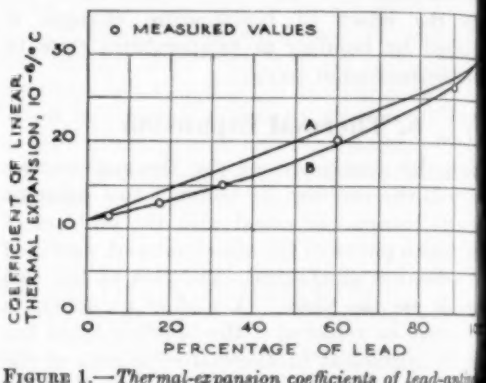

FIGURE 1.—*Thermal-expansion coefficients of lead-anti mixtures.*

Curve *A*. Percentage by weight calculation.
Curve *B*. Percentage by volume or stress equilibrium calculation.

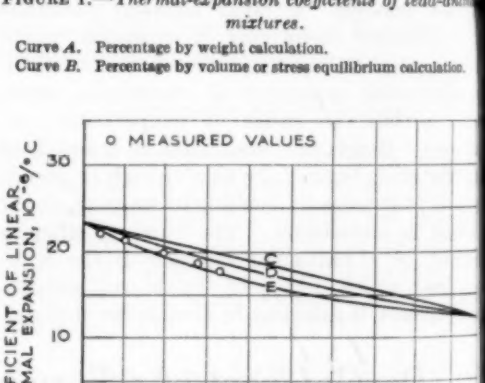

FIGURE 2.—*Thermal-expansion coefficients of beryllia aluminum alloys*

Curve *C*. Percentage by weight calculation.
Curve *D*. Percentage by volume calculation.
Curve *E*. Stress equilibrium calculation.

the same bulk moduli. If the ingredients have the same modulus to weight ratios, the calculation amounts to a percentage by weight interpolation.

Equation 6 has been verified with experimental values of several metallic mixtures. The thermal-expansion coefficients calculated according to equation 6 for several mixtures of lead and antimony and of beryllium [3] and aluminum are compared with the measured values in figures 1 and 2.

IV. Applications to Plastic Compositions

It has been found that the size and shape of the filler particles in plastic mixtures have an effect on the resultant coefficient of expansion of the mixture. The equations derived do not take this phenomenon into consideration. Difficulty is also encountered because the moduli of some materials are not available. To solve these problems, equation 6 is modified by substituting an empirically determined constant C for K/d for each material. Constant C is interpreted as proportional to the modulus-density ratio rather than being equal to it. The proportionality factor is dependent on the shape and size of the particles and on the distribution of the material in the matrix. It is assumed that the constant C for each specific filler and each plastic material is independent of the other components of a mixture if the ingredients are evenly distributed. This modified equation has been used successfully in several investigations. The use of this technique and the effects of the shape and size of fillers have been described in another report.[4]

In studies of the physical properties of reinforced plastics it has been found that the strongest materials were produced by oriented fibers in thermosetting resins. The material fabricated in this manner is essentially non-isotropic in all of its properties and has different coefficients of expansion depending on the direction of the fibers in the test specimen. Materials having isotropic properties can be obtained by random distribution or by planned orientation. The solution for any property must take into consideration the orientation of the filler as well as the percentage composition.

For a mixture whose components have nearly equal values of Poisson's ratio the bulk moduli are nearly proportional to the corresponding Young's moduli. For such mixtures Young's modulus may therefore be substituted for bulk modulus in equation 6 to yield the following expression for the thermal expansion coefficient of a mixture:

$$\alpha_r = \frac{\frac{\alpha_1 P_1 E_1}{d_1} + \frac{\alpha_2 P_2 E_2}{d_2} + \ldots + \frac{\alpha_n P_n E_n}{d_n}}{\frac{P_1 E_1}{d_1} + \frac{P_2 E_2}{d_2} + \ldots + \frac{P_n E_n}{d_n}}. \qquad (7)$$

Thus, in many cases where the bulk moduli are not available, equation 7 may be used instead of equation 6. The following experiments on a mixture of polystyrene and aluminum oxide illustrate the reasonably successful application of equation 7.

1. Application to a Mixture of Polystyrene and Aluminum Oxide

The applicability of the formula is illustrated by the behavior of brass inserts in a mixture of styrene resin with fused aluminum-oxide powder. Brass inserts in ordinary polystyrene cause the polystyrene to crack because of the different coefficients of thermal expansion. The coefficient of linear thermal expansion of polystyrene is approximately 70×10^{-6}/ deg C, that of brass is approximately 17×10^{-6}/ deg C.

Fused aluminum oxide was chosen for use in the mixture because it has a low coefficient of linear thermal expansion (8.7×10^{-6}/ deg C) and a high modulus of elasticity compared to its density. Its choice for use with polystyrene was also determined in part by its desirable electrical properties. There was no appreciable change in the excellent electrical resistance of polystrene when the aluminum-oxide filler was added. The data in table 1 for the coefficients of linear thermal expansion of mixtures of polystyrene and fused aluminum oxide, calculated according to the stress-equilibrium, formula show that approximately 90 percent of

[3] Mixtures of Be and Al apparently form a mechanical mixture, but no value for the bulk modulus or bulk compressibility was available. From the thermal coefficient, 17.8×10^{-6}/° C, of a known mixture containing 32.7 percent of Be and 66.3 percent of Al, and with reported densities and thermal coefficients of the ingredients, the bulk modulus of Be was calculated from equation 6 to be 15.2×10^{6} lb/ in ^{2}. From this value the thermal coefficients of other mixtures of Be and Al were calculated with the results shown in figure 2 in comparison with the reported values.

[4] Philip S. Turner, Jewel Doran, and Frank W. Reinhart, Fairing compositions for aircraft surfaces. NACA Technical Note No. 958 (November 1944)

polystyrene and 10 percent of aluminum oxide would be required to match the coefficient of linear thermal expansion of brass. As the coefficient of the particular brass used was not accurately known, and as it was thought better to err on the low side, 11 percent of aluminum oxide was used.

TABLE 1.—*Calculated coefficients of linear thermal expansion of mixtures of polystyrene and fused aluminum oxide*

Composition of mixture		Calculated coefficient of linear thermal expansion	
Fused aluminum oxide (Al_2O_3)	Polystyrene	By stress equilibrium formula (equation 7)	By rule of mixtures on percentage by volume basis
%	%	10^{-6}/°C	10^{-6}/°C
100	0	8.7	8.7
75	25	9.0	41.7
50	50	9.6	56.3
25	75	11.7	64.7
20	80	12.5	65.9
9.7	90.3	17	68.2
5	95	23.2	69.1
0	100	70	70

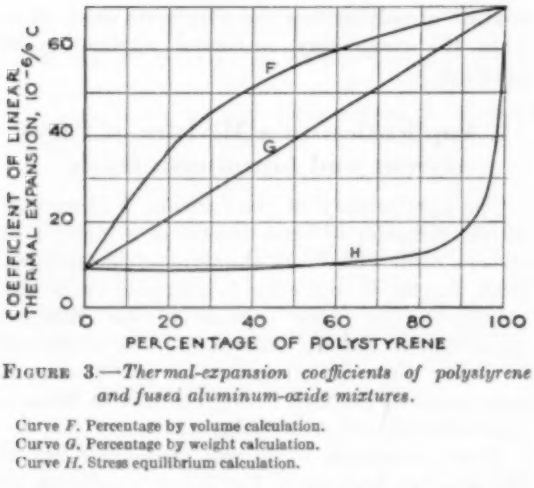

FIGURE 3.—*Thermal-expansion coefficients of polystyrene and fused aluminum-oxide mixtures.*

Curve *F*. Percentage by volume calculation.
Curve *G*. Percentage by weight calculation.
Curve *H*. Stress equilibrium calculation.

In figure 3, curve *F* represents the values of the coefficient of linear thermal expansion of mixtures of polystyrene and fused aluminum oxide calculated on a percentage by volume basis; curve *G*, on a percentage by weight basis; and curve *H*, by the stress-equilibrium formula (equation 7). Although the thermal coefficient of a mixture of 89 percent of polystyrene and 11 percent of fused aluminum oxide has not been measured, pieces molded with brass inserts show a radical difference between the behavior of pure polystyrene and the filled material. Analysis with polarized light indicates that there are stresses in the pure polystyrene concentrated at the boundaries between the brass and polystyrene, and these are sufficient to rupture the polystyrene. With 11 percent of fused aluminum-oxide filler no such stress concentrations occur, and there is no evidence that the filled styrene has fractured. The brass was sufficiently well bonded to the polystyrene mixture to permit sawing and machining of the composite material.

The conventional methods of calculation would yield for this composition a value of 63×10^{-6}/deg C for the coefficient of linear thermal expansion on a percentage by weight basis, which would indicate that the material should behave very nearly the same as the pure polystyrene. The behavior of the material, however, indicates that its coefficient is close to that of brass, which value was used to predetermine the composition by the use of the stress-equilibrium formula.

2. Application to Compositions for Filling Rivet Depressions

Rivet fillers for aluminum, used to cover depressions caused by riveting, have been tested by exposure to Washington weather for 1 year. An enigma developed when it was found that the composition having the best general weathering characteristics did not stand up the best in this application. The calculated values for coefficients of linear thermal expansion of the various compositions are as follows:

Material	*Calculated coefficient*
Cellulose nitrate + 25 percent of aluminum pigment	44.2×10^{-6}/deg C
Cellulose acetate butyrate + 25 percent of aluminum pigment	45.2×10^{-6}/deg C
Vinylite AYAF + 30 percent of aluminum pigment	30.6×10^{-6}/deg C

As the coefficient of linear thermal expansion of aluminum is 24×10^{-6}/deg C, the results are easily explained on the basis that composition 3, which happened to come closest to the coefficient of aluminum, gave the best bond.

Inasmuch as the lowest coefficient obtainable with aluminum pigment is 24×10^{-6}/deg C for 100-percent pigment, it becomes necessary to add another ingredient with a coefficient below aluminum to the plastic in order to obtain matched thermal coefficients. The following proportions

were calculated for cellulose-plastic compositions to reasonably match aluminum:

	Percent
Cellulose nitrate or cellulose acetate butyrate	66
Aluminum pigment	20
Fused aluminum oxide	14

Similarly, the following proportions were calculated for a vinyl acetate resin composition to match its coefficient of linear thermal expansion with that of aluminum:

	Percent
Vinylite AYAF resin	74.6
Aluminum pigment	20.0
Fused aluminum oxide	5.4

3. Application to mixtures of phenol-formaldehyde Resin and Glass Fibers

Approximate values for the properties of glass and phenol-formaldehyde resin required for use in the stress-equilibrium formula are as follows:

Young's modulus of elasticity:

For glass	11×10^6 lb/in^2.
For phenolic resin	1×10^6 lb/in^2.

Coefficient of linear thermal expansion:

For glass	7.44×10^{-6}/°C.
For phenolic resin	59×10^{-6}/°C.

Density (g/ml):

For glass	2.56
For phenolic resin	1.30

In order to simplify the calculation of the coefficients of linear thermal expansion of mixtures of these materials, equation 7 can be written in a form consolidating the physical constants:

$$a_r=\frac{a_1P_1+a_2P_2\ .\ .\ .+a_nP_n}{b_1P_1+b_2P_2\ .\ .\ .+b_nP_n}, \qquad (8)$$

in which a and b are constants for specific materials for a specific temperature range. The approximate values for these constants for the phenol-formaldehyde resin and glass calculated from the physical constants listed above are

	Glass	*Phenol-formaldehyde resin*
a	29.1	45.4
$b\times10^6$	3.91	0.77

In figure 4, curve I represents a percentage by weight interpolation for the glass-resin mixtures; curve J is calculated by the stress-equilibrium formula. Measured values of the coefficients of linear thermal expansion of two compositions shown in table 2 are plotted according to the percentage of the resin in the mixture. These samples contained approximately 4 percent of starch,

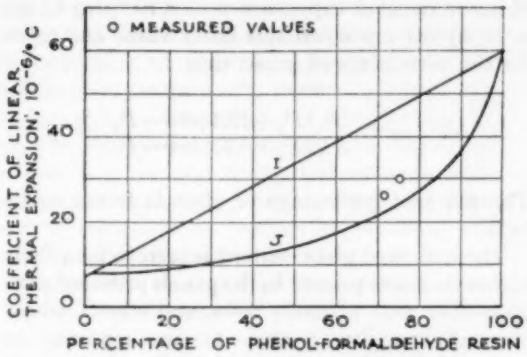

FIGURE 4.—*Thermal-expansion coefficients of phenol-formaldehyde resin and glass-fiber mixtures containing approximately 4 percent of starch.*

Curve I. Percentage by weight calculation (not including starch).
Curve J. Stress equilibrium calculation (not including starch).

which was neglected in calculating curve J. The theoretical coefficients for the compositions containing starch were not calculated because the required physical constants are not known. The experimental points fall much closer to the curve J calculated by the formula than to curve I. The curve on a percentage by weight basis would be similar to curve F in figure 3 and would be still further from predicting the actual result.

TABLE 2.—*Coefficients of linear thermal expansion of mixtures of glass fibers, phenolic resin, and starch*

Composition of mixture			Coefficient of linear thermal expansion	
Glass fiber	Phenol-formaldehyde resin (Bakelite XC-11749)	Starch	Calculated by stress equilibrium formula (equation 7)	Measured
%	%	%	10^{-6}/*deg C*	10^{-6}/*deg C*
100	0	----	7.44	----
50	50	----	14.2	----
25.2	70.8	4	----	26.0
25	75	----	23.6	----
22.2	73.8	4	----	29.9
10	90	----	37.4	----
0	100	----	60	----

The addition of metal faces to reinforced plastics may be desired in order to take advantage of the high-modulus properties of metals, as in an I-beam, or to obtain a facing impermeable to moisture. To do this effectively it would be necessary to have matched thermal-expansion coefficients in order to insure satisfactory bonds. To calculate the mixture of glass fiber and phenolic resin required to match aluminum alloy 24*S*, whose coefficient

of linear thermal expansion is 23×10^{-6}/deg C, let α_r in equation 8 equal this latter value and solve for the percentage of glass; thus

$$23\times10^{-6}=\frac{29.1P_g+45.4(100-P_g)}{3.91P_g+0.77(100-P_g)}10^{-6}.$$

The required percentage of glass is found to be 31.3.

The indicated glass content is seen to be a little higher than was present in the panels prepared with glass-fiber mat, phenolic resin, and starch, whose thermal-expansion coefficients are reported in table 4. These panels were fabricated between aluminum-alloy-24*S* faces. It was found possible to remove the metal face without seriously damaging it or the core material. The metal faces could not be removed from several other panels, having compositions closer to that calculated, without tearing the metal, shearing the metal at the bond, or rupturing the core.

The starch was added to these compositions in order to absorb the water in the ingredients or released by the resin during curing. It has been found difficult or impossible to produce plastic compositions with this phenolic-thermosetting resin at low pressures unless some water-absorbent material is present. Some of these glass-fiber panels were bonded at pressures as low as 50 lb/in.^{2}

V. Determination of Coefficients of Thermal Expansion of Plastics

In the early stages of the investigation an estimate of the coefficient of thermal expansion of the resin-bonded materials was obtained by the following method. Composite strips of one layer of metal and one of a fibrous material impregnated with the resin in varying proportions was pressed flat and cured at 150° C. The strips were then permitted to cool to room temperature. If the composite strip remained straight when cooled, it was considered that the thermal expansion of the plastic composition matched the metal. As the investigation proceeded, quantitative data for the coefficients of linear expansion of the resins were required.

The equipment used for this purpose consisted of two telescoping fused-quartz tubes, the inner tube being shorter than the outer and resting on the specimen. The expansion was measured by a dial gage, graduated to 0.0001 in., and fastened to the outer quartz tube with the measuring foot resting on the inner quartz tube, which in turn rested on the specimen. The temperature of the specimen was varied by immersing the quartz tubes containing the specimen in a water or an oil bath, heated with a hot plate, so that the rate of temperature rise of the bath was approximately 1 deg C per minute. The temperature of the specimen was measured by means of a potentiometer connected with a copper-constantan thermocouple, which was attached to the center of the specimen. Simultaneous measurements of temperature and extension were obtained by setting the potentiometer at predetermined points and recording the extension when no deflection was produced by opening or closing the circuit. The coefficient of linear expansion of the specimen was calculated from the temperature-extension curves. The results thus obtained were corrected for the expansion of the fused-quartz tubes by adding the coefficient of linear thermal expansion of fused quartz, 0.5×10^{-6}/deg C. Although this relatively rapid method does not insure a uniform temperature throughout the specimen, it presents a better picture of the changes taking place in the specimen which might be masked by changes in water content and by plastic flow at elevated temperatures, both of which would appreciably affect the results if the time of heating the specimen was prolonged. The stress on the specimen applied by the inner quartz tube and the micrometer foot did not exceed 10 lb/in.^{2}

The specimen used for thermal-coefficient measurements was a bar 6½ to 7½ in. long and about ½ in. wide. The thickness was that of the sheet from which the specimen was cut. Specimens for determination of the properties of both pure phenolic resin (Durez 120) and compositions of this resin containing filler were molded in the laboratory at 150° C and 1,000 lb/in.^{2} pressure. The length of the specimen was measured at room temperature to the nearest 0.01 in. with a steel scale. The specimens were rounded on the ends in order to obtain definite contact between the specimen and the apparatus over a small area. The position of the specimen with respect to the quartz tubes was maintained by washers near the ends of the spec-

which came in contact with the sides of the s but offered no appreciable resistance to ical motion of the specimen.

Measurements of the coefficient of linear nsion of an alloy using the method described ve are compared in table 3 with precision surements on a duplicate sample. The results not strictly comparable since the coefficient of r expansion of the sample changes slightly with heat treatment occurring during measurement. ause the time required to make the measure- ts differs in the two methods, the amount of aling that has occurred between measure- ts is different. The results, however, are ntially the same and indicate that the method loyed for the experimental work described in paper is quite reliable.

LE 3.—*Comparison of precision method and rapid thod of measuring coefficients of linear thermal expan- on*

Temperature range	Average coefficients of linear thermal expansion			
	Precision method *		Rapid method	
	First test	Repeat test	First test	Repeat test
°C	10^{-6}/deg. C	10^{-6}/deg. C	10^{-6}/deg. C	10^{-6}/deg. C
20 to 60	17.7	17.8	17.5	17.2
60 to 100	18.6	18.3	17.9	18.7
100 to 150	18.3	18.5	18.4	19.0
150 to 200	----	18.7	19.0	19.3
20 to 100	18.1	18.0	17.7	17.9
20 to 150	18.2	18.2	18.0	18.3
20 to 200	----	18.4	18.3	18.6

ata supplied by Division II-6. The cooperation of P. Hidnert in ying this information and other data represented graphically in figures 2 is gratefully acknowledged.

Factors Affecting Thermal-Coefficient Measurements of Plastics

Before considering the actual measurements, e of the factors peculiarly affecting the ther- l expansion and related properties of plastics uld be discussed. Organic plastic composi- ns, or water-absorbent materials, in general, in dition to the basic constituents, contain a tain amount of water which apparently acts same as an additional solid in the composition. great deal of the variation in the reported ues for the linear thermal expansion of wood is doubtedly related to differences in the water tent of the wood at the time of testing. In er to minimize such effects, all specimens tested in this investigation were initially conditioned at 25° C and 50-percent relative humidity.

The modulus of plastics varies considerably with change in temperature, particularly near the softening point. The range of temperature to which the reported values apply was chosen in each case to avoid large changes in water content and to avoid softening points. Each of these effects is indicated by breaks in temperature-extension and extension-time curves. Near the softening point of pure plastics the molding strains are relieved and dimensional changes occur which depend on the method of manufacture. These changes correspond to the dimensional changes encountered on aging. Reinforced or laminated materials also show changes in dimensions involving the relief of the thermal stresses set up by the differential coefficients of expansion of the resin and reinforcing medium. Prolonged heating at elevated temperatures causes shrinkage by the removal of water from the mixture. The relief of molding stresses seems to be permanent; the removal of water reversible.

2. Results of Thermal-Expansion Measurements for Plastics

Representative measurements of thermal-expansion coefficients of plastic materials for various temperature ranges are presented in table 4. A typical thermal-expansion curve for pure molded phenolic resin is shown in figure 5.

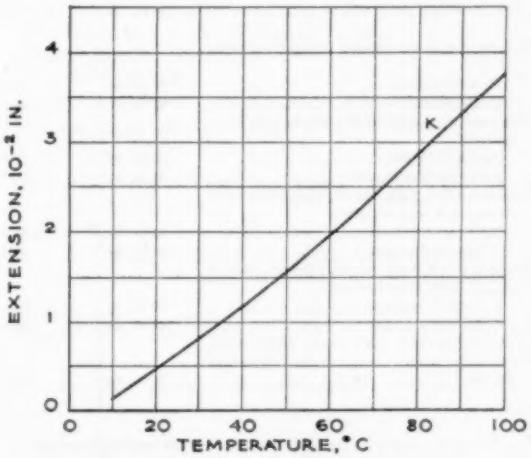

FIGURE 5.—*Thermal-expansion curve for pure molded phenolic resin, Durez 120.*

(Original length of specimen at room temperature: 7.05 in.).

TABLE 4 — *Measured coefficients of linear thermal expansion for various plastics*

Material [a]	Range	Linear thermal-expansion coefficient
	°C	10^{-4}/°C
Pure phenolic resin (Durez No. 120)	20 to 100	58.5 to 58.9
	20 to 50	49.7
	20 to 30	50.2
Durez No. 120, 10% Micronex (channel-type carbon black)	20 to 100	45.7 to 47.4
	20 to 100	44.9
Durez No. 120, 41% reagent-quality aluminum oxide	20 to 50	34.7
Durez No. 120, 10% lignin resin (first heating)	20 to 100	62.8
	53 to 100	78.8
	20 to 53	47.9
Durez No. 120, 10% lignin resin (second heating)	20 to 100	54.7
Durez No. 120, 10% lignin resin (third heating)	20 to 100	54.1
	20 to 53	47.2
	53 to 100	59.9
Durez No. 120, 10% walnut-shell-flour filler (first heating)	20 to 100	59.2
	49 to 100	68.0
	20 to 49	43.8
Durez No. 120, 10% walnut-shell-flour filler (second heating)	20 to 100	54.1
	49 to 100	58.8
	20 to 49	45.7
Glass Mat 25%, Bakelite XC-11749 phenolic resin 71%, starch 4%:		
First heating	20 to 65	29.9
Third heating	20 to 65	29.3
Glass Mat 28%, Bakelite XC-11749 68%, starch 4%	20 to 70	26.0
Glass Cloth 44%, Durez No. 120 39%, starch 17%	20 to 70	17.8
Columbia resin No. 39:		
First heating	10 to 50	103.3
Second heating	20 to 100	124.7
	20 to 50	105.8
Methyl-methacrylate resin	20 to 50	71.5
Pregwood P-5, parallel-ply maple,[b] low resin content:		
Parallel to grain	20 to 50	4.7
Perpendicular to grain	20 to 50	63.5
Pregwood P-1, parallel-ply maple, high resin content:		
Parallel to grain	20 to 50	5.9
Perpendicular to grain	20 to 50	68.7
Pregwood P-7, 7-ply maple, plies alternately crossed, low resin content:		
Four-ply direction	20 to 50	13.5
Three-ply direction	20 to 50	19.8
Pregwood P-3, 7-ply maple, plies alternately crossed, high resin content:		
Four-ply direction	20 to 50	16.7
Three-ply direction	20 to 50	21.0
Eight-ply 0.01-inch-thick birch, symmetrical cross-ply construction, 39.5% Amberlite PR-14	20 to 30	15.4

[a] Percentage figures are based on the weight of the total composition.

[b] These Pregwood materials (P-1 to P-8, inclusive) were erroneously reported to have been prepared with birch veneers in the NACA advance restricted report of July 1941, entitled "Properties of Reinforced Plastics and Plastic Plywoods."

Carbon black is frequently added to pl compositions as a filler. It is interesting there to note that the addition of 10 percent of a cha type of carbon black to phenol-formaldehyde r reduced the thermal coefficient of the mix approximately 20 percent (see table 4). F published values for the density and thermal- pansion coefficient of carbon black, together w the measured properties of the pure phenolic re a value for the bulk modulus of carbon black calculated to be approximately 3×10^6 lb/in.^{2}

Lignin resin is used in a number of applicati in conjunction with phenolic resins. Here i treated as a filler. Two effects are to be not first, that the product does not become st until it has been heated a considerable lengt time beyond the time required to cure the phen resin; and second, that the lignin initially incre the coefficient of the mixture but after hea finally decreases it by a small amount.

The effect of the walnut-shell flour is simila that of the lignin resin. The manufacturer this material state that it contains a large pro tion of lignin. One of the uses of this materi as an extender for plywood adhesives.

The behavior of filled phenol-formaldeh resin containing 25 percent of glass fiber, 71 per of phenolic resin, and 4 percent of starch, is il trated by the curves for mixtures of glass fi and phenolic resin shown in figure 6. Curve and *O* are for pure phenol-formaldehyde resin glass fibers, respectively. Curve *N* was obtai on the first heating cycle. The form of the cu above 70° C is affected by plastic flow, relief molding strains, and further curing of the re The weight of the inner fused-quartz tube and pressure of the micrometer foot contribute some the force producing plastic flow. The shrinka indicated at 100° C on curve *N* took place ove period of 5 hours, during which time the tempe ture was maintained constant. The rate of shri age was initially rapid but reached a steady va after about 4 hours. After cooling the sam slowly and then reheating to 100° C the sa steady rate of shrinkage was resumed for 4 ad tional hours, after which the specimen was slo cooled to room temperature. The total shrinka amounted to 0.5 percent. Curve *M* of figure the thermal-expansion curve for this anneal specimen.

The transparent materials for which data given in table 4 have been used or proposed

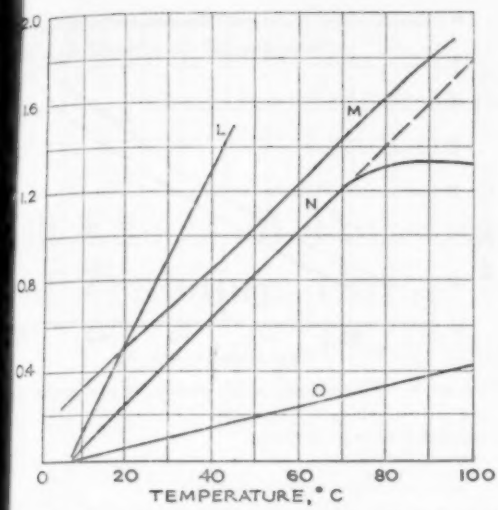

FIGURE 6.—*Thermal-expansion curves for phenolic resin and glass fiber mixtures.*

(Original length at 25° C: 6.57 in.; final length at 25° C: 6.54 in.).
Curve *L*. Pure phenolic resin.
Curve *M*. Filled phenolic, third heating.
Curve *N*. Filled phenolic, first heating.
Curve *O*. Glass mat (manufacturer's data).

e as airplane windshields. The temperature-tension curves in each case varied from a ooth curve on the first heating cycle between ° and 100° C. The curve for the Columbia esin 39 sample (fig. 7, curve *P*) showed a decrease expansion in this range followed by a resumption the upward trend. No such break occurred the cooling curve (fig. 7, curve *Q*) or in the rve obtained when the sample was heated a cond time (fig. 7, curve *R*), although the tem-

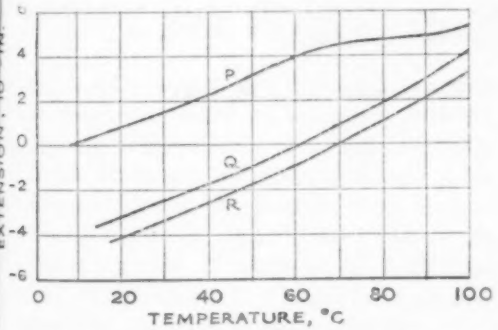

FIGURE 7.—*Thermal-expansion curves for Columbia Resin No. 39.*

(Original length at room temperature: 7.48 in.).
Curve *P*. First heating.
Curve *Q*. First cooling.
Curve *R*. Second heating.

perature was raised above 110° C. The sample was permanently shortened during the first heating to the extent of 0.5 percent. The specimen at the same time increased in thickness. The curve for methyl-methacrylate resin (fig. 8, curve *S*) for the range 50° to 100° C showed an increase in expansion followed by a decrease. Again the break did not occur in the cooling curve (fig. 8, curve *T*). The changes were too small to be measured significantly with a steel scale, so a check was run on smaller specimens that were heated in an oven at 80° C for 18 hours. The indicated change was verified by an increase in dimensions in the plane of the sheet and a decrease in thickness. This is in agreement with observed dimensional changes on aging. Methyl-methacrylate resin is one of the best available materials from the standpoint of freedom from crazing, unless subjected to strain, and dimensional stability. The surfaces of both materials appeared to be unaffected by the treatment.

TABLE 5.—*Coefficients of linear thermal expansion and moduli of elasiicity of Pregwoods*

Material	Measured values [a]		Calculated values	
	Modulus of elasticity in tension	Coefficient of linear thermal expansion for the range 20° to 50° C	Modulus of elasticity in tension	Coefficient of linear thermal expansion for the range 20° to 50° C
HIGH RESIN CONTENT. PARALLEL-PLY MATERIAL (P-1)				
	10^6 lb/in.^{2}	10^{-6}/°C	10^6	10^{-6}/°C
Parallel to grain	3.70	5.9		
Perpendicular to grain	.84	68.7		
HIGH RESIN CONTENT. CROSS-PLY MATERIAL, SEVEN PLY (P-3)				
Parallel to three-ply direction	2.04	21.0	2.07	20.5
Parallel to four-ply direction	2.29	16.7	2.47	15.0
LOW RESIN CONTENTS. PARALLEL-PLY MATERIAL (P-5)				
Parallel to grain	3.97	4.7		
Perpendicular to grain	.68	63.5		
LOW RESIN CONTEND. CROSS-PLY MATERIAL, SEVEN PLY (P-7)				
Parallel to three-ply direction	2.17	19.8	2.09	15.6
Parallel to four-ply direction	2.52	13.5	2.56	11.4

[a] The values given for the coefficient of linear thermal expansion are those obtained on the first heating cycle.

The Pregwood samples listed in table 4 were submitted by the Formica Insulation Co. and were cut from the same sheets as the test specimens reported upon in NACA Advance Restricted Report of July 1941, entitled "Properties of Reinforced Plastics and Plastic Plywoods." The modulus data reported at that time for parallel-ply material may be used with the measured thermal coefficients to calculate the thermal coefficients of the cross-ply material. The modulus of the cross-ply material may also be calculated as a composite column using the data for the parallel-ply materials. It is assumed, perhaps erroneously, that the "high" and "low" resin designations indicate definite resin contents. The calculated and observed values for the several properties are shown in table 5.

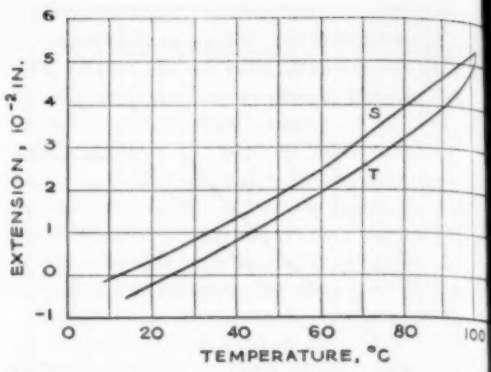

FIGURE 8.—*Thermal-expansion curves for cast methacryl resin.*

(Original length at 25° C: 7.04 in.).
Curve *S*. Heating.
Curve *T*. Cooling.

VI. Conclusions

The implications of the concept and methods of analysis touched briefly in the preceding pages are too numerous to be adequately treated in so short a space. Special applications have been mentioned throughout the paper. Some general conclusions are presented in the following paragraphs.

Stable bonds are possible between large sections if the thermal coefficients of the component parts are matched. The bond under such conditions is not seriously affected by extreme temperature changes.

The method of computing the thermal coefficients of mixtures is applicable to mixtures in general and particularly applicable to problems of reinforced plastics.

Since the magnitude of the stresses distributed throughout the mixture is proportional to the size of the elements, the ultimate strength of the material and its fatigue limits should be raise by reducing particle size. Specifically, the streng of plywood should be increased by the use of th veneers. At the temperature of fabrication th effect of particle size should reach a minimum

It should be possible to formulate pigmente protective coatings which will have improved ad hesion to the coated materials by the use of th thermal-coefficient formula. The thermal-coeffi cient method described in this paper offers a rapi and reliable means of obtaining the basic physica data needed for use in the calculations. Wit such information the proper combination of ma terials can be calculated to yield a film matchin the base material with respect to coefficient o thermal expansion.

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alt Effects of Potassium Nitrate, Sodium Sulfate, nd Trisodium Citrate on the Activity Coefficients of *p*-Phenolsulfonate Buffers

By Roger G. Bates, Pauline T. Diamond, Murray Eden, and S. F. Acree

Electromotive-force measurements of cells without liquid junction that contained hydrogen and silver–silver-chloride electrodes and alkaline *p*-phenolsulfonate buffers with added salts of different valence types were made from 0° to 60° C. The 63 buffer solutions studied were prepared by the partial neutralization of potassium *p*-phenolsulfonate with sodium hydroxide, and each contained approximately equal molal amounts of potassium *p*-phenolsulfonate and of potassium sodium *p*-phenolate sulfonate. These solutions were classified into five series on the basis of the kind of added salt and the ratio, R, of its molality to the molality of each buffer salt, as follows: Potassium nitrate, $R=1$; sodium sulfate, $R=1$; sodium sulfate, $R=0.5$; barium chloride, $R=0.5$; trisodium citrate, $R=0.33$. All the buffers, with the exception of the series to which barium chloride was added, likewise contained sodium chloride, $R=1$. The ionic strengths of the solutions varied from 0.05 to 0.8.

The values of the second dissociation constant of *p*-phenolsulfonic acid given in an earlier paper were confirmed. The influence of potassium nitrate, sodium sulfate, and trisodium citrate on the activity coefficient term, $f_{Cl}f_{HP_s}/f_{P_s}$, in which f represents an activity coefficient on the molal scale and the subscripts represent respectively chloride ion and the primary and secondary anions of the buffer, was determined for solutions containing no sodium chloride at 0° to 35° C. No pronounced differences in character were observed among the effects of the salts of the three valence types in concentrations sufficient to make up one-fifth of the ionic strength of the mixture.

I. Salt Effect on the pH of Buffered Solutions

Addition of a neutral salt to a buffer solution omposed of the primary and secondary salts of a eak dibasic or polybasic acid normally results in n increase in the acidity of the solution. Inadquate knowledge of the activity coefficients in ixtures of electrolytes and of their role in the ehavior of a system in homogeneous equilibrium owever, often makes it impossible to predict uantitatively the effect of salt on the pH.

The pH of a buffer composed of potassium -phenolsulfonate (KHPs) and of potassium odium *p*-phenolate sulfonate (KNaPs) can be xpressed by the mass-law equation in loga-

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rithmic form, with the appropriate activity coefficients, as follows:

$$pH = pK - \log\ (m_{HPs}/m_{Ps}) - \log(f_{HPs}/f_{Ps}),\ (1)$$

where pK is the negative of the common logarithm of the dissociation constant of the phenol group of *p*-phenolsulfonic acid on the molal scale, m represents molality (moles/1,000 g of water), and f is the activity coefficient on the corresponding scale. It is evident that the change of pH with addition of neutral salt to a phenolsulfonate buffer must result largely from changes in the activity coefficients of the two anions of the buffer.

The change in pH when salt is added to the buffer solution is called the total salt effect. If provision is made for the effect of hydrolysis upon the molal ratio (second term on the right of eq 1), and the molalities of the components of the buffer remain unaltered, the change of the last term of eq 1 upon addition of salt measures the total salt effect.

It may reasonably be supposed that the change of the activity-coefficient term when the ionic strength of the solution changes at constant buffer ratio as a result of a variation in buffer concentration alone can be expressed by an equation such as the following:

$$\log \frac{f_{HPs}}{f_{Ps}} = \frac{3A\sqrt{\mu}}{1+Ba\sqrt{\mu}} + \beta\mu, \qquad (2)$$

where A and B are constants of the Debye-Hückel equation, μ is the ionic strength, and a and β are parameters characteristic of the mixture of ions. The values of a and β evidently control the rate of change of log (f_{HPs}/f_{Ps}) with ionic strength and, hence, the total salt effect. When neutral salt is added to a buffer solution, the character of the variation of the activity-coefficient term with ionic strength may be unaffected. On the other hand, a and β may change as a result of interactions of the buffer ions with those of the salt, and the variation with ionic strength will then be different.

The total salt effect, therefore, can be of two types. The effect of salt addition is of the first type when the change of pH produced is the same as would normally result from an increase in ionic strength of the buffer alone, without the introduction of foreign ions or molecules. Thus, the pH of the mixture of buffer and salt will be the same as that of a more concentrated buffer of the same ionic strength and buffer ratio, without added salt. In other words, the rate of change of the activity coefficient term with ionic strength remains unaltered when a neutral salt is substituted for a amount of buffer mixture which contributes the same increment to the ionic strength.

The second type of salt effect is the result specific or abnormal interactions among the ions of the mixture. In the extreme case, these interactions may alter not only the activity coefficient of the buffer ions but their concentrations as well. Polar compounds, polymers, or complex ions may even be formed. These effects cause the activity coefficient term to change in an abnormal manner with changing ionic strength. As a result, the pH of the buffer with salt differs from that of a pure buffer solution of the same ionic strength and buffer ratio.

In most cases, the effect of salt is probably the more general second type. Furthermore, the term log (f_{HPs}/f_{Ps}) at constant ionic strength may reasonably be expected to vary linearly with composition of the solution. When the kinds of ions added are similar to those of the buffer, however, it is possible that they will alter the activity-coefficient term by the same amount as would the buffer ions, added in like quantity. A salt effect of the second type may, of course, appear to be of the first type when the amount of salt added is small compared with the ionic strength of the buffer itself.

The problem of determining salt effects on the phenolsulfonate buffer is resolved into a determination of the changes in the activity coefficients on addition of salt. Unfortunately, the ratio of the activity coefficients of the primary and secondary anions, f_{HPs}/f_{Ps}, cannot readily be measured. In this investigation, the character of the salt effect of potassium nitrate, sodium sulfate, and trisodium citrate on the activity coefficients of these ions was studied by evaluating the activity coefficient term, $f_{HPs}/f_{Cl}/f_{Ps}$, in buffered solutions of sodium chloride with and without one of the three neutral salts. In order that the observed effect might represent as closely as possible the influence of the salt on the buffer ions alone, the activity-coefficient term was evaluated in the limit of zero sodium chloride from 0° to 35° C.

Electromotive-force measurements at 0° to 60° C were made with buffer mixtures composed of sodium chloride and approximately equal molal amounts of potassium *p*-phenolsulfonate and

tassium sodium *p*-phenolate sulfonate without ded salt, and for similar buffers which contained tassium nitrate, sodium sulfate, or trisodium rate. One series contained barium chloride stead of sodium chloride. The effects of the ree alkali salts of different valence types on the tivity coefficients were found to be approxitely the same when the added salt made up one-fifth of the total ionic strength. The emf data for these buffer solutions with added salt, together with those for the series of buffers that contained chloride, confirm the values for the second dissociation constant of *p*-phenolsulfonic acid found in an earlier study [1].[1]

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Method of Evaluating the Effect of Salts on the Activity Coefficients

Electromotive-force measurements of cells of the pe

$$\text{Pt-H}_2\,|\,\text{KHPs}(m_1);\ \text{KNaPs}(m_2);\ \text{NaCl}(m_3);\ \left.\begin{matrix}\text{KNO}_3\\ \text{Na}_2\text{SO}_4\\ \text{BaCl}_2\\ \text{Na}_3\text{C}_6\text{H}_5\text{O}_7\end{matrix}\right\}(m_4)\,|\,\text{AgCl-Ag} \qquad \text{(I)}$$

ere made at intervals of 5 degrees from 0° to ° C. The chemical changes that result from awing a finite current from this cell are given the complete cell reaction,

$$1/2\text{H}_2+\text{AgCl}+\text{Ps}^-=\text{Ag}+\text{Cl}^-+\text{HPs}^-, \qquad (3)$$

which the standard free energy change, $-\Delta F^{\circ *}$,

$$-\Delta F^{\circ *}=E^{\circ *}F=RT\ln K^*, \qquad (4)$$

here $E^{\circ *}$ is the potential of the hypothetical cell f type I, in which each of the components has activity of unity; K^* is the thermodynamic quilibrium constant for eq 3; and R, T, and F re the gas constant, the absolute temperature, nd the faraday.

The total reaction in the cell may be written in wo parts. The first of these is the electrode eaction,

$$1/2\text{H}_2+\text{AgCl}=\text{Ag}+\text{H}^++\text{Cl}^-;\ -\Delta F_1^\circ=E^\circ F, \qquad (5)$$

here E° is the standard potential of the cell, $H_2|HCl|AgCl$-Ag, and the other is a homogeneous quilibrium that involves the hydrogen ion formed y the electrode reaction, namely, the equilibrium etween the primary and secondary anions of henolsulfonic acid,

$$\text{HPs}^-=\text{H}^++\text{Ps}^-;\ -\Delta F_2^\circ=RT\ln K. \qquad (6)$$

The constant K in eq 6 is the thermodynamic econd dissociation constant for the acid. It has een determined by Bates, Siegel, and Acree [1] over the range of temperatures from 0° to 60° C. From eq 4, 5, and 6 it is evident that

$$E^{\circ *}=E^\circ-(RT/F)\ln K$$
$$=E^\circ+(2.3026\,RT/F)\text{p}K, \qquad (7)$$

where pK is the negative of the common logarithm of K. Values of E° at 0° to 60° C have been recalculated by Hamer, Burton, and Acree [2] from the emf data of Harned and Ehlers [3].

The relation between emf, E, and the molalities and activity coefficients of the reactants and products of the cell reaction is

$$\frac{E-E^{\circ *}}{k}+\log\frac{m_{\text{HPs}}m_{\text{Cl}}}{m_{\text{Ps}}}=-\log\frac{f_{\text{HPs}}f_{\text{Cl}}}{f_{\text{Ps}}}, \qquad (8)$$

where k is written for $2.3026\,RT/F$. The activity-coefficient term in the equilibrium constant for reaction 3 can be computed from the emf by eq 8. By observing the behavior of the emf and, through it, the activity-coefficient term when neutral salts of different valence types are added to the buffered chloride solutions, information can be gained regarding the nature of the effect of added salt on the three ions involved in the cell reaction.

In solutions that contained neutral salts, as in buffered chloride solutions without added salts [4], the experimental values of the last term of eq 8 could be represented satisfactorily by an equation of the type

$$\log\frac{f_{\text{HPs}}f_{\text{Cl}}}{f_{\text{Ps}}}=\frac{2A\sqrt{\mu}}{1+Ba^*\sqrt{\mu}}+\beta^*\mu, \qquad (9)$$

derived from the Debye-Hückel theory. Inasmuch as a confirmation of the value of pK was desired, a^* and β^* were evaluated as before [1] from the graphs used to derive this constant by extrapolation of the values of pK', the negative logarithm of the "apparent" dissociation constant, to an ionic strength of zero.

pK' is defined through a combination of eq 7, 8, and 9:

$$pK' = pK - \beta^* \mu = \frac{E - E^\circ}{k} + \log \frac{m_{HPs} m_{Cl}}{m_{Ps}} + \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}}. \quad (10)$$

In the range of temperatures from 0° to 35° C, a^* and β^* were also determined for phenolsulfonate buffers with and without neutral salt at several different concentrations of sodium chloride. The values of these parameters were plotted as a function of m_{NaCl}/μ, the fractional contribution of sodium chloride to the ionic strength, and the corresponding values, a° and β°, in the absence of sodium chloride were obtained by extrapolation. The value of the activity-coefficient term in the limit of zero sodium chloride, f_a°, is defined by

$$\log f_a^\circ \equiv \log \left[\frac{f_{HPs} f_{Cl}}{f_{Ps}} \right]_{m_{Cl}=0} = \frac{2A\sqrt{\mu}}{1 + Ba^\circ\sqrt{\mu}} + \beta^\circ \mu. \quad (11)$$

It is impossible to compute the change of p[H] upon addition of salt to the buffer solution fr[om] the measured change in f_a° without recourse to [an] arbitrary assumption regarding the relative mag[ni]tudes of the individual activity coefficients. Th[e] parameters a° and β° might, for example, [be] identified with a and β of eq 2, or a relation such [as] $\log f_{Cl} = -(1/3) \log (f_{HPs}/f_{Ps})$, based upon valen[ce] effects in very dilute solutions, be introduced. The influence of neutral salt on $\log f_a^\circ$ should, however, approximate in character the salt effe[ct] on the buffer anions alone. From these result[s] therefore, an estimate could be made of (a) th[e] magnitude of the change in the activity-coefficien[t] term of eq 1 when small concentrations of salt ar[e] added to the buffer and (b) whether salts of di[f]ferent types produce markedly different effect[s] on the pH, apart from their different contribution[s] to the ionic strength.

III. Experimental Procedures and Results

The buffer solutions were made by the weight dilution of stock solutions that were prepared in quantities of two liters each from weighed amounts of potassium *p*-phenolsulfonate and a standard solution of carbonate-free sodium hydroxide. Each stock solution, with the exception of the one to which barium chloride was added, also contained both sodium chloride and one of the three neutral salts[2] chosen for study. The specific conductance of the water was in most cases about 0.5×10^{-6} mho.

The potassium phenolsulfonate analyzed 100.10 percent by titration with alkali. The sodium chloride was part of the same fused sample used in earlier work on phenolsulfonate buffers [1, 4]. It was found by titration with acid to contain 0.007 percent by weight of free alkali. This amount of impurity changes the emf of the cell by less than 0.01 mv and can safely be ignored. Description of the equipment, methods of preparing the electrodes, and other experimental details have been given elsewhere [1, 5].

The emf data for cell I are given in the sections to follow. In each of the 63 buffers, m_1 and m_2 were approximately equal. When sodium chloride was present, its molality was usually nearly th[e] same as that of each buffer salt, except in series [E] where the ratio of chloride to buffer was varie[d]. The ratio, R, of m_4 to m_1 was approximately unit[y] for solutions that contained potassium nitrat[e] 1 and 0.5 for sodium sulfate, and 0.33 for trisodiu[m] citrate. Sodium chloride was absent from seri[es] D, and barium chloride ($R = 0.5$) was present.

The combined experimental errors in the com[po]sitions of the solutions and in the emf measure[-]ments, together with the errors in the values [of] the natural constants and the standard potentia[ls] are thought not to exceed 0.18 mv at any tem[-]perature. The uncertainty from these source[s] amounts to 0.003 in the activity-coefficient term of eq 9 or eq 11.

1. Buffers With Added Potassium Nitrate

Potassium nitrate of reagent quality was re[-]crystallized once from water and dried to con[-]stant weight at 110° C. Preliminary experi[-]ments showed that satisfactory results could b[e] obtained with the hydrogen electrode in solution[s] that contained nitrate ion in moderate concentra[-]tion in a phenolsulfonate buffer at a pH of 8.[2] The hydrogen electrodes in solutions containin[g] 0.06- to 0.1-*m* potassium nitrate, however, oc[-]

[2] A neutral salt is considered here to be one that has no appreciable buffer capacity at pH 8.4 to 9.2. Inasmuch as hydrogen and silver-silver-chloride electrodes were used, chlorides, bromides, iodides, sulfides, and substances readily reduced by hydrogen in alkaline solution were excluded.

ionally gave erratic potentials and had to be laced. No larger differences between the ini- and final emf at 25° C were found, however, h nitrates than with other salts, and the dilute utions were satisfactory in every respect. e emf results for 1:1 buffers with added potas- m nitrate are given in table 1.

BLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), sodium chloride (m_3), and potassium nitrate (m_4)*

[m_2=0.9785m_1; m_3=0.9349m_1; m_4=0.9332m_1]

tion number	m_1	$E_0°$	$E_5°$	$E_{10}°$	$E_{15}°$	$E_{20}°$	$E_{25}°$
	0.10830	0.78654	0.78003	0.79339	0.79676	0.79998	0.80319
	.08572	.79168	.79534	.79874	.80232	.80571	.80910
	.04450	.80721	.81123	.81510	.81896	.82238	.82675
	.03591	.81270	.81690	.....	.82457	.82856	.83260
	.02520	.82172	.82609	.83027	.83450	.83856	.84263
	.013753	.83706	.84176	.84626	.85079	.85511	.85958
	.011864	.84087	.84559	.85019	.85476	.85927	.86374
	.008651	.84873	.85352	.85844	.86319	.86785	.87258

	$E_{30}°$	$E_{35}°$	$E_{40}°$	$E_{45}°$	$E_{50}°$	$E_{55}°$	$E_{60}°$
	.....	.....	0.80932	0.81264	0.81570	0.81901	0.82204	0.82503
	.....	.....	.81558	.81904	.82217	.82555	.82879	.83211
	0.83042	.....	.....	.83732	.84114	.84516	.84885	.85248
	.83659	.....	.84407	.84785	.85188	.85562	.85932	.85930
	.84670	.85055	.85454	.85859	.86261	.86654	.87046	
	.86392	.86801	.87253	.87670	.88096	.88512	.88930	
	.86821	.87239	.87697	.88121	.88510	.88982	.89409	
	.87725	.88157	.88635	.89177	.89534	.89977	.90423	

Buffers with added sodium sulfate

Sodium sulfate, of the grade designated "for rogen determination", was recrystallized twice m water. The water of hydration was removed drying the salt in a vacuum oven at tempera- e up to 100° C and at 130° C under atmospheric ssure. Two ratios of anhydrous sodium sul- e to buffer were studied. The buffers of series contained approximately equal molal amounts sodium sulfate and of each buffer salt, whereas five solutions in series C contained one-half as ch added salt as buffer. The emf values at to 60° C are given in table 2.

Buffers with Added Barium Chloride

Measurements were made of one series of phenol- lfonate buffers in which barium chloride was bstituted for sodium chloride. The method out- ed earlier in this paper obviously cannot serve determine the salt effect of barium chloride on

TABLE 2.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), sodium chloride (m_3), and sodium sulfate (m_4).*

[Solutions B1 to B5: m_2=0.9916m_1; m_3=0.9425m_1; m_4=0.9727m_1. Solutions B6 to B11: m_2=1.0150m_1; m_3=0.9512m_1; m_4=0.9554m_1. Solutions B12 to B20: m_2=0.9803m_1; m_3=0.9455m_1; m_4=0.9444m_1. Series C: m_2=0.9743m_1 m_3=0.9413m_1; m_4=0.4732m_1]

Solution number	m_1	$E_0°$	$E_5°$	$E_{10}°$	$E_{15}°$	$E_{20}°$	$E_{25}°$
B1	0.10686	.....	.....	.....	.....	.....	0.80234
B2	.06602	.....	.....	.....	.....	.....	.81520
B3	.05438	.....	.....	.....	.....	.....	.82054
B4	.02030	.....	.....	.....	.....	.....	.84785
B5	.010524	.....	.....	.....	.....	.....	.86636
B6	.10443	0.78644	0.78993	0.79333	0.79672	0.80007	.80339
B7	.06808	.79660	.80032	.80407	.80772	.81130	.81490
B8	.04623	.80907	.81007	.81393	.81776	.82154	.82535
B9	.02709	.81939	.82377	.82793	.83205	.83619	.84030
B10	.013336	.83763	.84232	.84684	.85134	.85580	.86027
B11	.013036	.83798	.84271	.84725	.85172	.85620	.86073
B12	.10722	.78516	.78866	.79216	.79557	.79872	.80207
B13	.08036	.79189	.79553	.79918	.80281	.80618	.80965
B14	.06067	.79879	.80261	.80641	.81012	.81365	.81731
B15	.04181	.80796	.81197	.81598	.81993	.82366	.82749
B16	.02823	.81766	.82190	.82612	.83029	.83430	.83832
B17	.015906	.83247	.83701	.84148	.84597	.85028	.85462
B18	.014489	.83486	.83941	.84393	.84844	.85280	.85719
B19	.009284	.84621	.85099	.85579	.86055	.86506	.86970
B20	.006629	.85475	.85963	.86459	.86953	.87434	.87927
C1	.08524	.79022	.79431	.79789	.80125	.80490	.80833
C2	.05903	.79965	.80367	.80743	.81098	.81469	.81842
C3	.03767	.81078	.81504	.81908	.82277	.82677	.83072
C4	.018541	.82872	.83313	.83786	.84195	.84629	.85057
C5	.010837	.84253	.84733	.85199	.85666	.86122	.86582

	$E_{30}°$	$E_{35}°$	$E_{40}°$	$E_{45}°$	$E_{50}°$	$E_{55}°$	$E_{60}°$
B1	0.80569	0.80883	.....	.....	.....	.....	.....
B2	.81876	.82234	.....	.....	.....	.....	.....
B3	.82420	.82782	.....	.....	.....	.....	.....
B4	.85207	.85634	.....	.....	.....	.....	.....
B5	.87092	.87542	.....	.....	.....	.....	.....
B6	.80676	.81002	0.81330	0.81652	0.81973	0.82287	0.82609
B7	.81852	.82201	.82551	.82895	.83235	.83576	.83914
B8	.82912	.83284	.83655	.84016	.84375	.84741	.85097
B9	.84440	.84838	.85237	.85631	.86020	.86407	.86792
B10	.86467	.86903	.87336	.87768	.88196	.88616	.89038
B11	.86508	.86948	.87389	.87802	.88213	.88634	.89016
B12	.80535	.80861	.81193	.81508	.81827	.82140	.82450
B13	.81308	.81656	.82000	.82330	.82669	.83001	.83332
B14	.82087	.82444	.82805	.83155	.83501	.83844	.84189
B15	.83128	.83506	.83885	.84252	.84621	.84986	.85351
B16	.84238	.84637	.85036	.85424	.85814	.86200	.86583
B17	.85894	.86321	.86756	.87177	.87597	.88012	.88425
B18	.86157	.86589	.87025	.87449	.87872	.88290	.88704
B19	.87430	.87886	.88344	.88788	.89232	.89672	.90098
B20	.88391	.88862	.89313	.89774	.90238	.90703	.91143
C1	.81175	.81512	.81854	.82192	.82524	.82855	.83184
C2	.82199	.82561	.82923	.83275	.83628	.83975	.84325
C3	.83450	.83841	.84224	.84601	.84971	.85346	.85710
C4	.85480	.85892	.86311	.86726	.87139	.87551	.87956
C5	.87031	.87485	.87931	.88373	.88814	.89248	.89679

the properties of the buffer anions alone, for it is impossible to obtain the activity-coefficient term at zero ratio of chloride to buffer and maintain, at the same time, a constant ratio of buffer to added salt. A series of measurements of solutions containing barium chloride was considered desirable, however, to aid in determining pK as accurately as possible.

Barium chloride, of reagent grade, was purified by recrystallization from water, powdered, and dried at 125° C. The emf data for phenolsulfonate buffers with added barium chloride are given in table 3.

TABLE 3.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenosulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), and barium chloride (m_4)*

[m_2=0.9854m_1; m_4=0.5092m_1]

Solution number	m_1	$E_9°$	$E_8°$	$E_{12}°$	$E_{13}°$	$E_{14}°$	$E_{15}°$
D1	0.07950	0.79066	0.79435	0.79801	0.80128	0.80489	0.80844
D2	.07455	.79223	.79596	.79964	.80303	.80665	.81018
D3	.05521	.79950	.80349	.80733	.81096	.81470	.81838
D4	.03890	.80821	.81229	.81632	.82022	.82412	.82801
D5	.03033	.81469	.81885	.82295	.82702	.83104	.83513
D6	.02901	.81556	.81979	.82394	.82802	.83203	.83606
D7	.018064	.82779	.83226	.83666	.84092	.84527	.84958
D8	.015583	.83163	.83621	.84073	.84509	.84948	.85381
D9	.012138	.83800	.84263	.84722	.85171	.85622	.86070
D10	.009828	.84626	.85110	.85590	.86054	.86523	.86983
		$E_{16}°$	$E_{17}°$	$E_{18}°$	$E_{19}°$	$E_{20}°$	$E_{21}°$	$E_{22}°$
D1		0.81183	0.81518	0.81868	0.82198	0.82528	0.82864	0.83198
D2		.81366	.81702	.82053	.82390	.82724	.83059	.83390
D3		.82205	.82564	.82925	.83280	.83632	.83979	.84324
D4		.83188	.83566	.83951	.84325	.84696	.85072	.85428
D5								
D6		.84008	.84399	.84793	.85183	.85569	.85951	.86326
D7		.85380	.85794	.86215	.86629	.87039	.87442	.87848
D8		.85816	.86253	.86659	.87060	.87495	.87911	.88319
D9		.86516	.86952	.87394	.87827	.88256	.88680	.89102
D10		.87449	.87901	.88350	.88798	.89242	.89683	.90104

4. Buffers with added trisodium citrate

In the search for a neutral salt that would yield trivalent ions, trisodium citrate was chosen. A preparation of the salt, of reagent grade, was crystallized from water and dried to constant weight at 130° C.

The pH change when small amounts of sodium hydroxide were added to a 0.05-m solution of trisodium citrate was determined with the use of thymol blue. The pH was found to increase from 8.4 to 9.0 upon the addition of 5×10^{-5} mole of the alkali to a liter of the citrate solution. Thus, m_1/m_2 for a 0.1-m phenolsulfonate buffer initially

TABLE 4.—*Electromotive forces of hydrogen–silver-chlo cells containing mixtures of potassium p-phenolsulfo (m_1), potassium sodium p-phenolate sulfonate sodium chloride (m_3), and trisodium citrate (m_4).*

[m_2=0.9888m_1; m_3=0.9521m_1; m_4=0.3334m_1]

Solution number	m_1	$E_9°$	$E_8°$	$E_{12}°$	$E_{13}°$	$E_{14}°$	
E1	0.10611	0.78854	0.78907	0.79242	0.79582	0.79903	0.8
E2	.08339	.79134	.79498	.79855	.80209	.80549	.8
E3	.07267						
E4	.05579	.80101	.80487	.80867	.81236	.81598	.8
E5	.04833	.80458	.80864	.81241	.81626	.81996	.8
E6	.02841	.81779	.82208	.82628	.83042	.83441	.8
E7	.02052	.82627	.83072	.83505	.83934	.84345	.8
E8	.010988	.84187	.84670	.85136	.85608	.86049	.8
E9	.007951	.85041	.85529	.86013	.86488	.86932	.8
E10	.005326						
		$E_{15}°$	$E_{16}°$	$E_{17}°$	$E_{18}°$	$E_{19}°$	$E_{20}°$	
E1		0.80590	0.80855	0.81178	0.81523	0.81840	0.82145	0.8
E2		.81243	.81591	.81930	.82263	.82586	.82927	.8
E3								
E4		.82363	.82726	.83085	.83441	.83795	.84147	.8
E5		.82747	.83111	.83478	.83858	.84213	.84557	.8
E6		.84270	.84666	.85062	.85460	.85852	.86239	.8
E7		.85193	.85607	.86021	.86431	.86839	.87233	.8
E8		.86971	.87421	.87871	.88317	.88749	.89175	.8
E9		.87910	.88375	.88833	.89295	.89742	.90197	.9
E10								

TABLE 5.—*Electromotive forces of hydrogen–silver-chlo cells containing mixtures of potassium p-phenolsulfo (m_1), potassium sodium p-phenolate sulfonate (m_2), added neutral salt (m_4), and varying molalities of so chloride (m_3)*

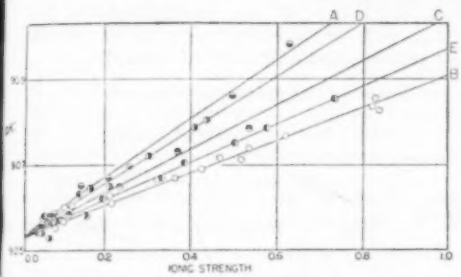
Solution number	m_1	m_2	m_3	m_4 (KNO_3)	$E_9°$	
F1	0.04300	0.04300	0.02589	0.04310	0.81868	0.8
F2	.04300	.04309	.016602	.04310	.82957	.8
F3	.04300	.04309	.008233	.04310	.84599	.8
				m_4 (Na_2SO_4)		
F4	.04300	.04309	.02557	.04310	.81869	.8
F5	.04300	.04309	.015982	.04310	.82770	.8
F6	.04300	.04309	.008634	.04310	.84410	.8
F7	.04300	.04309	.005038	.04310	.84997	.8
				m_4 ($Na_3C_6H_5O_7$)		
F8	.04300	.04309	.02510	.014367		
F9	.04300	.04309	.016448	.014367	.82930	.8
F10	.04300	.04309	.008340	.014367	.84547	.8
		$E_{10}°$	$E_{11}°$	$E_{12}°$	$E_{13}°$	$E_{14}°$	
F1		0.82726	0.83168	0.83565	0.83951	0.84350	0.8
F2		.83832	.84278	.84698	.85102	.85534	.8
F3		.85544	.86020	.86473	.86914	.87359	.8
F4		.82699	.83130	.83531	.83921	.84328	.8
F5		.83824	.84299	.84719	.85118	.85556	.8
F6		.85342	.85824	.86276	.86712	.87161	.8
F7		.85540	.86203	.86471	.86912	.87368	.8
F8		.82791	.83223	.83630	.84025	.84443	.8
F9		.83812	.84274	.84701	.85114	.85541	.8
F10		.85486	.85964	.86420	.85863	.87312	.8

pH 9.0 could be changed only 0.1 percent by ding 0.05 mole of trisodium citrate to a liter buffer. This change corresponds to 0.0004 in and pK, or 0.02 mv in emf. For the mixtures series E, in which the ratio of molality of the odium citrate to that of each buffer salt was 3, the correction is even smaller.

The experimental data at 0° to 60° C for mixtures containing trisodium citrate are listed in table 4. The results for solutions containing potassium nitrate (R=1), sodium sulfate (R=1), and trisodium citrate (R=0.33), with varying ratios of sodium chloride to buffer, are given in table 5.

IV. Second Dissociation Constant of *p*-Phenolsulfonic Acid

Values of pK, the negative of the common arithm of the second dissociation constant at of the phenol group) of *p*-phenolsulfonic acid re derived from the measurements of the solu- ns in series A, B, C, D, and E by the method scribed in an earlier section. Figure 1 is a plot the values of pK' at 25° C as a function of ionic ength for all five series. In table 6, the values α^* that gave the best straight line for extrapola-



URE 1.—*Plots of* pK' *as a function of ionic strength at 25° C.*

letters indicate the series marking (tables 1 to 4) ◒=series A; ○=series =series C; ◑=series D; ◐=series E.

BLE 6.—*Values of* a^* *and* β^* *for five series of phenolsulfonate buffers at 0° to 60° C*

	Series A, KNO_3		Series B, Na_2SO_4		Series C, Na_2SO_4		Series C, $BaCl_2$		Series E, $Na_3C_6H_5O_7$	
	a^*	$-\beta^*$	a^*	$-\beta^*$	a^*	$-\beta^*$	a^*	$-\beta^*$	a^*	$-\beta^*$
°C										
	8.0	0.106	8.5	0.052	8.3	0.061	7.7	0.086	8.5	0.057
	8.0	.100	8.5	.046	8.3	.066	7.7	.082	8.5	.054
	8.0	.091	8.4	.046	8.2	.062	7.6	.080	8.4	.050
	8.0	.087	8.4	.042	8.1	.051	7.6	.067	8.4	.045
	8.0	.078	8.3	.039	8.1	.049	7.5	.070	8.3	.042
	8.0	.072	8.2	.036	8.0	.051	7.5	.065	8.2	.044
	8.0	.059	8.1	.037	8.0	.043	7.5	.060	8.2	.041
	8.0	.052	8.0	.036	8.0	.043	7.5	.057	8.2	.036
	8.0	.048	8.0	.034	8.0	.040	7.5	.057	8.2	.034
	8.0	.046	8.0	.030	8.0	.039	7.5	.051	8.2	.030
	8.0	.039	8.0	.027	8.0	.037	7.5	.049	8.2	.026
	8.0	.040	8.0	.030	8.0	035	7.5	.049	8.2	.024
	8.0	.032	8.0	.027	8.0	.032	7.5	.047	8.2	.022

tion and of β^*, the negative of the slope of this line, are listed for each series at each of the 13 temperatures.

The value of m_{OH} required for the hydrolysis correction was obtained conveniently from the emf data without the usual successive approximations by the relation [1]:

$$\log m_{OH} = (E - E^\circ)/k + \log m_{Cl} - pK_w, \quad (12)$$

where pK_w is the negative logarithm of the ionization constant of water. When m_{OH} was needed for buffers other than those for which emf data were available, it was computed from the approximation

$$m_{OH} \approx (K_w/K)/(m_1/m_2). \quad (13)$$

Values of K_w/K at 0° to 60° C are tabulated in the earlier paper [1]. Use of this approximate expression for m_{OH} introduces an error of about 0.002 unit in the pH of the 0.005-m phenolsulfonate buffer at 60° C. The error decreases rapidly as the temperature is lowered or the concentration of buffer is increased. The ionic strength, μ, and buffer ratio, m_{HPs}/m_{Ps}, are readily computed, with the aid of m_{OH}, by the equations

$$\mu = m_1 + 3m_2 + m_3 + nm_4 - m_{OH} \quad (14)$$

and

$$m_{HPs}/m_{Ps} = (m_1 + m_{OH})/(m_2 - m_{OH}). \quad (15)$$

The added salts were assumed to be completely ionized.[3]

A value of pK was computed from the emf measurement of each buffer solution at each temperature by eq 10 with the aid of a^* and β^* obtained by graphical means. The summary of pK (table 7) demonstrates the essential agree-

[3] As the added salt (with the exception of barium chloride) takes no part in the cell reaction, an exact knowledge of its molality is unnecessary. If 5 percent of this added salt were undissociated, the change in ionic strength would be insufficient to alter log ($f_{HPs}f_{Cl}/f_{Ps}$) by 0.001, as can be shown with the aid of eq 9 or table 8. The value of n accordingly was assumed to be 1 for potassium nitrate, 3 for barium chloride and sodium sulfate, and 6 for trisodium citrate.

ment between the mean of the results of this investigation at each temperature with pK reported earlier [1]. The mean difference is less than 0.001 unit. At the higher temperatures, however, the deviations of each series from the mean are occasionally as large as 0.002 or 0.003. In general, the solutions containing potassium nitrate or barium chloride were found to yield lower values of pK than did those to which sodium sulfate or trisodium citrate had been added. In view of the acceptable agreement between the two measurements of pK, no recalculation of the thermodynamic constants for the dissociation of phenolsulfonate ion was made. Values of $E^{\circ *}$ computed by eq 7 are given in the last column of the table.

TABLE 7.—*Summary of values of* pK *for the second dissociation of p-phenolsulfonic acid and* $E^{\circ *}$ *at 0° to 60° C*

t	Series A, KNO_3	Series B, C, Na_2SO_4	Series D, $BaCl_2$	Series E, $Na_3C_6H_5O_7$	Mean	RP1539	$E^{\circ *}$
°C							Jc
0	9.3541	9.3528	9.3498	9.3524	9.352	9.352	0.7
5	9.2836	9.2841	9.2818	9.2830	9.284	9.284	.7
10	9.2203	9.2201	9.2187	9.2206	9.220	9.220	.7
15	9.1606	9.1612	9.1593	9.1593	9.160	9.160	.7
20	9.1038	9.1052	9.1033	9.1034	9.104	9.105	.7
25	9.0527	9.0540	9.0514	9.0534	9.053	9.053	.7
30	9.0052	9.0063	9.0038	9.0053	9.005	9.005	.7
35	8.9585	8.9626	8.9591	8.9618	8.961	8.961	.7
40	8.9190	8.9221	8.9176	8.9205	8.920	8.921	.7
45	8.8805	8.8853	8.8811	8.8849	8.883	8.883	.7
50	8.8480	8.8520	8.8472	8.8511	8.850	8.849	.7
55	8.8144	8.8183	8.8143	8.8195	8.817	8.816	.7
60	8.7868	8.7888	8.7845	8.7884	8.787	8.787	.7

V. Effect of Neutral Salts on the Activity Coefficients

With the aid of a^* and β^* from table 6, a calculation of log $(f_{HPs}f_{Cl}/f_{Ps})$ was made by eq 9, in order to compare the values of this term at several ionic strengths and at temperatures of 0°, 25°, and 60° C. The results are shown in table 8, where data for phenolsulfonate-chloride solutions without added salt are also given. For the latter, a^* is 8.0, and β^* at 0°, 25°, and 60° C has the values −0.079, −0.057, and −0.038 [4].

The change of the activity-coefficient term with the addition of neutral salt when the ionic strength remains unaltered is small, particularly at 25° C and higher temperatures.[4] In these concentrations, therefore, the added salts probably effect no large change in the electrostatic character of the buffer medium. The small effect of salt is evident in figure 2, where the activity-coefficient term and $(E-E^{\circ})/k+\log(m_{HPs}m_{Cl}/m_{Ps})$ are plotted as a function of the square root of the ionic strength.

1. Buffer Solutions Without Added Salt

A determination of the effect of a changing ratio of sodium chloride on a^* and β^* was reported earlier [4]. As in the present work, the 1:1 phenolsulfonate buffer was studied by means of emf measurements at 0° to 60° C. The value of

TABLE 8.—*Values of the activity-coefficient term,* $(f_{HPs}f_{Cl}/f_{Ps})$, *in phenolsulfonate-chloride mixtures with and without added salts at 0°, 25°, and 60° C.*

The molal proportions, HPs:Ps:NaCl: added salt, are:
Column 2; 1:1:1:0. Column 5; 1:1:0:0.5.
Columns 3 and 4; 1:1:1:1. Column 6; 1:1:1:0.33.

Ionic strength	log $(f_{HPs}f_{Cl}/f_{Ps})$ for solutions containing—				
	No added salt	KNO_3	Na_2SO_4	$BaCl_2$	$Na_3C_6H_5O_7$
TEMPERATURE 0° C					
0.02	0.099	0.099	0.098	0.100	0.
.05	.134	.133	.133	.136	.
.1	.162	.159	.160	.164	.
.2	.186	.181	.185	.189	.
.3	.197	.189	.198	.200	.
.5	.204	.191	.208	.207	.
.6	.204	.188	.210	.206	.
TEMPERATURE 25° C					
0.02	0.104	0.104	0.104	0.105	0.
.05	.140	.140	.140	.143	.
.1	.170	.169	.170	.174	.
.2	.198	.195	.199	.203	.
.3	.211	.207	.213	.218	.
.5	.223	.216	.230	.230	.
.6	.225	.217	.234	.232	.
TEMPERATURE 60° C					
0.02	0.111	0.111	0.111	0.112	0.
.05	.150	.150	.150	.153	.
.1	.182	.183	.183	.187	.
.2	.214	.215	.216	.219	.
.3	.230	.232	.233	.236	.
.5	.247	.250	.252	.253	.
.6	.251	.255	.258	.258	.

[4] Nims [6] has determined $-\log(f_{Cl}f_{HG}/f_G)$, where G represents the singly charged glycolate anion, in glycolate buffer solutions containing chloride and has found a pronounced salt effect. Three series of solutions, in which the cation was respectively potassium, lithium, and barium, gave quite different values for the activity-coefficient term.

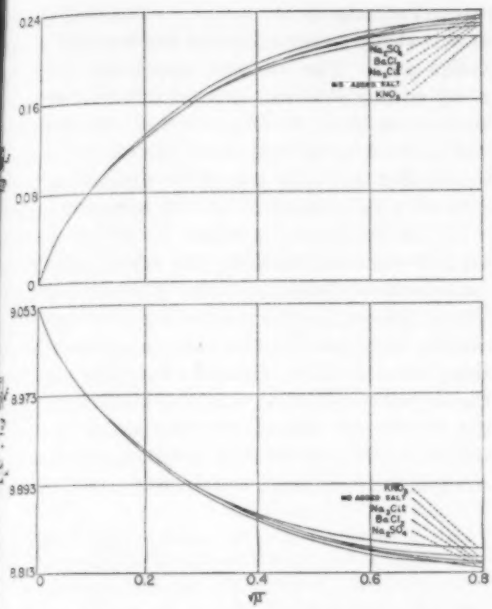


FIGURE 2.—*Salt effect on the activity-coefficient term (upper curve) and on* $(E-E^\circ)/k+\log(m_{HP}m_{Cl}/m_{P_a})$ *(lower curve) at 25° C. Compare eq 9 and 10.*

a^* was found to be 8.0 A at all temperatures and to be substantially unchanged when the molal ratio of sodium chloride to each buffer salt was reduced from unity to one-tenth. The parameter β^* was negative and changed in a regular manner as the temperature was increased.

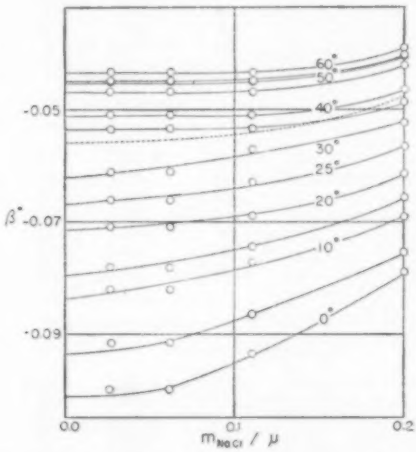


FIGURE 3.—*Plots of* β^* *as a function of* m_{NaCl}/μ *for 1:1 phenolsulfonate buffers with varying amounts of sodium chloride.*

Figure 3 shows the change of β^* with the ratio of sodium chloride to buffer salt. The limiting values, β°, are given in table 9. The value of a° is 8.0 A at each temperature.

TABLE 9.—*Values of* a° *and* β° *for 1:1 phenolsulfonate buffers without added salt and for buffers containing potassium nitrate, sodium sulfate and trisodium citrate (molality of added neutral salt)/(molality of each buffer salt)* $=1$ (KNO_3); $1(Na_2SO_4)$; *and* $1/3(Na_3C_6H_5O_7)$.

t	Without added salt		KNO_3		Na_2SO_4		$Na_3C_6H_5O_7$	
	a°	β°	a°	β°	a°	β°	a°	β°
°C								
0	8.0	−0.101	8.0	−0.098	8.5	−0.046	8.5	−0.058
5	8.0	−.094	8.0	−.087	8.5	−.046	8.5	−.058
10	8.0	−.085	8.0	−.078	8.4	−.046	8.4	−.058
15	8.0	−.080	8.0	−.070	8.4	−.046	8.4	−.058
20	8.0	−.072	8.0	−.063	8.3	−.046	8.3	−.058
25	8.0	−.066	8.0	−.058	8.2	−.046	8.2	−.058
30	8.0	−.063	8.0	−.052	8.1	−.046	8.2	−.058
35	8.0	−.053	8.0	−.048	8.0	−.046	8.2	−.058
40	8.0	−.051						
45	8.0	−.047						
50	8.0	−.045						
55	8.0	−.045						
60	8.0	−.043						

2. Buffer Solutions With Added Salt

The interdependence of a^* and β^* is noteworthy.[5] It is ordinarily difficult, in view of the normal experimental error of a series of points, to establish the correct value of a^* within 0.1 to 0.2 A by choice of the value that yields the best straight line. An error of this magnitude in a^* is, fortunately, offset almost completely by a compensatory change in β^*. For example, if 8.2 A were chosen for a^*, instead of 8.0 A, in the mixtures with varying amounts of sodium chloride but without added neutral salt, the plot of β^* at 25° C with respect to the fractional contribution of sodium chloride to the ionic strength would follow the dashed line of figure 3, and β° would be assigned a value of −0.056 instead of −0.066. With the use of $a^\circ=8.2$ and $\beta^\circ=-0.056$, $\log f_\pm$ for the 0.1-m buffer (ionic strength of 0.4) calculated from eq 11 would be 0.2157 instead of 0.2154 at 25° C, and at an ionic strength of 0.01, the difference would be 0.0006.

Advantage was taken of this agreement in

[5] Van Rysselberghe and Eisenberg [7] and Robinson and Harned [8] have suggested modifications of the Hückel equation, in which a single parameter expresses successfully the activity coefficient of the alkali halides and hydrogen halides up to concentrations of 1 to 4 m.

determining the limiting parameters for buffers that contained neutral salt in the absence of sodium chloride. For the complete analysis of the data of series F given in table 5, it was not necessary to have an independent measure of a^* for each ratio of sodium chloride to buffer and neutral salt. Such a determination would require the study of several dilutions of each mixture of series F. Instead, a^* for the appropriate mixture of buffer and salt was selected from table 6, pK' was computed for each solution at each temperature, and β^* was evaluated from the relation,

$$\beta^* = (pK - pK')/\mu. \quad (16)$$

Plots of β^* as a function of m_{NaCl}/μ were constructed, and β°, the intercept for zero concentration of sodium chloride, was found. Five experimental points determined the extrapolation for solutions that contained sodium sulfate, whereas measurements that represented four different ratios of sodium chloride to buffer were available for solutions with potassium nitrate and trisodium citrate. The limiting parameters for the mixtures containing neutral salt are given in table 9, together with those for the 1:1 buffer without added salt. The data for solutions with varying contents of sodium chloride did not extend above 35° C. The parameter β° has constant values of -0.046 and -0.058, within 0.004, for the mixtures with sodium sulfate and trisodium citrate, respectively, in this range of temperatures. The limiting values of β^* are thought to be correct to ± 0.006. This uncertainty corresponds to an error of 0.003 in the activity-coefficient term at an ionic strength of 0.5.

It is now possible, with eq 11 and the constants given in table 9, to compute $\log f_B^*$ for 1:1 phenolsulfonate buffers that contain potassium nitrate or sodium sulfate in molalities equal to that of each buffer salt, or trisodium citrate in one-third the molality of the buffer. Furthermore, the value of this activity-coefficient term is likewise known for the same buffer in the absence of salt. The change which results from adding a single definite amount of each of three neutral salts of different valence types to a 1:1 phenolsulfonate buffer has therefore been determined, but the effect of other concentrations of salt, larger or smaller than this one, is still unknown. Inasmuch as the effect on the pH of relatively small amounts of salt is of most concern in the preparation and use of accurate pH standards, the molality of neutral salt used in this study never exceeded the molality of each buffer salt. The changes produced in a° and β° by adding sufficient neutral salt to increase the ionic strength 25 to 75 percent above that of the buffer alone is not large, and the effects produced by smaller amounts would be difficult to determine without a refinement of the experimental method.

In the solutions for which a° and β° listed in table 9 were determined, the added neutral salt contributed different amounts to the ionic strength. These amounts were one-fifth for potassium nitrate, three-sevenths for sodium sulfate, and one-third for trisodium citrate. In order to obtain the activity-coefficient term for mixtures in which the added salt contributed the same fraction of the ionic strength in each instance, the measured changes were reduced, as necessary, to place them

TABLE 10.—*Salt effects on the activity-coefficient term in the absence of sodium chloride; values of log f_B^* (eq 11) for 1:1 phenolsulfonate buffers with and without added neutral salts at 0°, 25°, and 35° C*

The added salts contribute one-fifth of the ionic strength in each case

Ionic strength	log f_B^* for buffer solutions containing—			
	No added salt	KNO_3	Na_2SO_4	Na_3Cit
	TEMPERATURE 0°C			
0.02	0.099	0.099	0.098	0.0
.05	.133	.133	.133	.1
.1	.160	.160	.160	.1
.2	.182	.183	.183	.1
.3	.191	.192	.194	.1
.4	.194	.195	.198	.1
.5	.193	.195	.199	.1
	TEMPERATURE 25°C			
.02	0.104	0.104	0.103	0.1
.05	.140	.140	.140	.1
.1	.169	.170	.169	.1
.2	.196	.198	.197	.1
.3	.209	.211	.210	.2
.4	.215	.219	.217	.2
.5	.219	.223	.221	.2
	TEMPERATURE 35°C			
.02	0.106	0.106	0.106	0.1
.05	.143	.143	.143	.1
.1	.173	.174	.174	.1
.2	.202	.203	.203	.2
.3	.216	.217	.217	.2
.4	.224	.226	.225	.2
.5	.229	.231	.230	.2

n a common basis, in direct proportion to the fractional contribution of the salt to the ionic strength. The largest of the measured salt effects was 0.018, found when sodium sulfate ($R=1$) was present at 0° C and an ionic strength of 0.5. In view of the relatively small effects involved, this procedure for computing the effect of amounts of salt smaller than those actually used was considered justifiable.[6] A comparison of log f_H° for solutions in which the added salt makes up one-fifth of the total ionic strength is given in table 10. No specific effects larger than the uncertainty of measurement are apparent in the data of table 10. The effectiveness of salts of the 1–1, 1–2, and 1–3 valence types at equal ionic strengths in altering the activity coefficients is nearly the same, and no marked abnormal influence of the increased ionic charge is evident. Furthermore, the salt effect of each of the three salts is no larger than the combined uncertainties inherent in the determination of β° and in the experimental measurements, or 0.006 at an ionic strength of 0.5. Changes larger than the estimated limits of error are found, as expected, for mixtures in which sodium sulfate and trisodium citrate contribute more than one-fifth of the ionic strength.

If, indeed, the change of log f_H° with addition of neutral salt approximates in character the behavior of log ($f_{H_2PO_4}/f_{PO_4}$), it can be concluded that the effect of neutral salts in moderate concentrations on the pH of phenolsulfonate buffer solutions is governed primarily by the increase in ionic strength and not by the specific nature of the salt itself. When the added salt makes up one-fifth or less of the ionic strength, the pH of the solution is close to that of a solution of the pure buffer of the same total ionic strength.[7]

[6] By analogy with mixtures of strong electrolytes, log f_H° at a given ionic strength is expected to vary in an approximately linear manner with change of composition, provided that the contribution of the salt to the ionic strength of the mixture is plotted. For a review of this topic, see chapter 15 of the monograph by Harned and Owen [9].

[7] Evidently the effect of salts on the negative of the common logarithm of the activity of hydrogen ion will be quite different from the change produced in $-\log m_H$ or $-\log c_H$, often considered to measure the salt effect on the pH (see, for example, reference 10). In general, addition of salt to a dilute solution of a weak acid causes m_H to increase and f_H to decrease. Hence, the product of these two quantities, the activity, may change less than does the concentration alone.

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